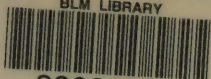


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# PARAHO OIL SHALE DEMONSTRATION

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## LABORATORY REPORT

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FINAL REPORT  
VOLUME 4







#15703728

Paraho

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1976

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## FOREWORD

Under a lease approved by a BLM Library of the United States in May, 1972, Paraho undertook a demonstration project with the federal government, to demonstrate the feasibility of the Paraho processes and hardware for retorting oil shale. This Final Report to participants of the Paraho Oil Shale Demonstration is a six-volume document that describes the research and development operations, laboratory design and cost estimating, and the commercial evaluation studies carried out from late-1972 to mid-1976.

## PARAHO FINAL REPORT

## LABORATORY

## VOLUME 4

THIS VOLUME 4, AUGUST 23, 1976, IS PREPARED UNDER THE TERMS OF THE PARTICIPANTS AGREEMENT WITH PARAHO CORPORATION AND DEVELOPMENT ENGINEERING, INC. MOREOVER, BECAUSE OF THE COMMITMENT TO THE GOVERNMENT NOT TO PUBLISH INFORMATION PREPARED BY PARTICIPATION SHOULD BE STRICTLY CONTROLLED ON A NEED-TO-KNOW BASIS UNTIL AFTER THIS MATERIAL HAS BEEN PUBLISHED BY THE GOVERNMENT OR PARAHO DEVELOPMENT ENGINEERING, INC.

The field operations were conducted at the Devil Points Oil Shale Research Facilities located on the Devil Oil Shale Reserves near Rifle, Colorado. One of these leased facilities was transferred from the Bureau of Mines (BOM) to the Energy Research and Development Administration (ERDA) when the latter agency was formed in 1974.

The Paraho Oil Shale Demonstration was privately sponsored by the following seventeen participants at a total cost of \$9.4 million:

Sohio Petroleum Company  
Southern California Edison Company  
The Cleveland-Cliffs Iron Company  
Gulf Oil Corporation

STANDARD  
D-2222, BUILDING CO  
BANKERS BUILDING  
P. O. BOX 1000  
NEW YORK, N. Y. 10003-0001





## FOREWORD

Under a lease approved by the President of the United States in May, 1972, Paraho undertook, in cooperation with the federal government, to demonstrate the engineering, economic and environmental feasibility and desirability of the Paraho processes and hardware for retorting oil shale. This Final Report to participants of the Paraho Oil Shale Demonstration is a six-volume document that describes the research and development operations, the engineering design and cost estimating, and the commercial evaluation studies carried out from late-1973 to mid-1976.

THIS VOLUME 4 IS CONSIDERED CONFIDENTIAL UNDER THE TERMS OF THE PARTICIPANTS AGREEMENTS WITH PARAHO CORPORATION AND DEVELOPMENT ENGINEERING, INC. MOREOVER, BECAUSE OF THE COMMITMENT TO THE GOVERNMENT NOT TO PUBLISH INFORMATION PREMATURELY, DISTRIBUTION SHOULD BE STRICTLY CONTROLLED ON A NEED-TO-KNOW BASIS UNTIL AFTER THIS MATERIAL HAS BEEN PUBLISHED BY THE GOVERNMENT OR PARAHO.

The field operations were conducted at the Anvil Points Oil Shale Research Facilities located on the Naval Oil Shale Reserves near Rifle, Colorado. Administration of these leased facilities was transferred from the Bureau of Mines (BOM) to the Energy Research and Development Administration (ERDA) when the latter agency was formed in 1974.

The Paraho Oil Shale Demonstration was privately sponsored by the following seventeen participants at a total cost of \$9.4 million:

- Sohio Petroleum Company
- Southern California Edison Company
- The Cleveland-Cliffs Iron Company
- Gulf Oil Corporation



FORWORD

Under a lease approved by the President of the United States in May, 1952, Paraho undertook, in cooperation with the Federal Government, to demonstrate the engineering, economic and environmental feasibility and desirability of the Paraho processes and hardware for retorting oil shale. This final Report to participants of the Paraho Oil Shale Demonstration is a six-volume document that describes the research and development operations, the engineering design and cost estimating, and the commercial evaluation studies carried out from late-1952 to mid-1956.

THIS VOLUME 4 IS CONSIDERED CONFIDENTIAL UNDER THE TERMS OF THE PARTICIPANTS AGREEMENTS WITH PARARO CORPORATION AND DEVELOPMENT ENGINEERING, INC. MOREOVER, BECAUSE OF THE COMMITMENT TO THE GOVERNMENT NOT TO DISSEMINATE INFORMATION PRESENTED, DISTRIBUTION SHOULD BE STRICTLY CONTROLLED ON A NEED-TO-KNOW BASIS UNTIL AFTER THIS MATERIAL HAS BEEN EVALUATED BY THE GOVERNMENT OR PARARO.

The field operations were conducted at the Naval Point Oil Shale Research Facilities located on the Naval Oil Shale Reserve near Rifle, Colorado. Administration of these leased facilities was transferred from the Bureau of Mines (BOM) to the Energy Research and Development Administration (ERDA) when the latter agency was formed in 1954.

The Paraho Oil Shale Demonstration was privately sponsored by the following seventeen participants at a total cost of \$2.4 million:

Sonic Petroleum Company  
Southern California Edison Company  
The Cleveland-Cliffs Iron Company  
Gulf Oil Corporation





Arthur G. McKee and Company  
Kerr-McGee Corporation  
Shell Development Corporation  
Standard Oil Company (Indiana)  
The Carter Oil Company (Exxon)  
Mobil Research and Development Corporation  
Webb-Gary-Chambers-McLorraine (Group)  
Sun Oil Company  
Texaco Inc.  
Phillips Petroleum Company  
Atlantic Richfield Company  
Marathon Oil Company  
Chevron Research Company

These participants received the right to license Paraho's oil shale technology on favorable terms for their support and cooperation which are gratefully acknowledged.

The results of Paraho's operations at Anvil Points are encouraging. They demonstrate that the process works, that the equipment is operable and durable, that thermal efficiencies and yields are high, and that the entire system developed is environmentally acceptable. The extended periods of Paraho retort operations and the results obtained demonstrate this. The evidence includes the 77-day Pilot Plant run and the 56-day Semi-Works run, both of which were terminated voluntarily.

After the 56-day retort run, 10,000 barrels of Paraho crude shale oil were shipped to the nearby Gary Western Refinery and converted into military products. This federally funded work was done for the U.S. Navy's Energy and Natural Resources Research and Development Office. That Office coordinated the refining and the nationwide, refined product testing program and publishing a report entitled:



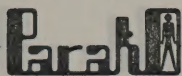
- Arthur G. Moore and Company
- Kerr-McGee Corporation
- Shell Development Corporation
- Standard Oil Company (Indiana)
- The Gaffet Oil Company (Exxon)
- Mobil Research and Development Corporation
- Webb-Gary-Chambers-McLaurine (Group)
- Sun Oil Company
- Texas Inc.
- Phillips Petroleum Company
- Atlantic Richfield Company
- Northern Oil Company
- Chevron Research Company

These participants received the right to license Paraho's oil shale technology on favorable terms for their support and cooperation which are gratefully acknowledged.

The results of Paraho's operations at Naval Pointe are encouraging. They demonstrate that the process works, that the equipment is operable and durable, that thermal efficiencies and yields are high, and that the entire system developed is environmentally acceptable. The extended periods of Paraho test operations and the results obtained demonstrate this. The evidence includes the 77-day Pilot Plant run and the 55-day Semi-works run, both of which were terminated voluntarily.

After the 55-day test run, 10,000 barrels of Paraho crude shale oil were shipped to the nearby Gary Western Refinery and converted into refinery products. This federally funded work was done for the U.S. Navy's Energy and Natural Resources Research and Development Office. That Office coordinated the refining and the subsequent, refined product testing program and publishing a report entitled:





Production and Refining of 10,000 Bbl. Paraho Crude  
Shale Oil Into Military Fuels, U. S. Navy Contract  
#N0014-75-C-0055

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A retorted shale management research project jointly funded by the Bureau of Mines and Paraho will be completed in late-1976 at an estimated additional cost of \$0.5 million. At that time, a report entitled, "Retorted Shale Management", will be issued as the concluding volume of this report.

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Production and Refining of 10,000 Bbl. Paraho Crude  
Shale Oil Into Military Fuels, U. S. Navy Contract

470014-75-C-0035

A reformed shale management research project jointly funded by the Bureau of Mines and Paraho will be completed in late-1976 at an estimated additional cost of \$0.5 million. At that time, a report entitled, "Reformed Shale Management", will be issued as the concluding volume of this report.



## PARAHO LABORATORY

## Final Report

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**1. STATISTICS**

**2. LABORATORY  
PROCEDURES**





## I. STATISTICS

This section of the final report is divided into four portions - sample load, laboratory equipment, precision, and accuracy. This section, more than any other, illustrates the growth curve or the evolving nature of the Paraho project.

This evolution is most evident in the sample load both in the number and nature of samples obtained and tests run. Data in Table I-A-1 show this growth trend. The year 1974 consisted largely of initial start-up and growth. It was not until the last five full months of operation that the laboratory was operating at peak efficiency. During that period, nearly 24000 tests were completed on nearly 5000 samples. Routine samples included only those sampled routinely during retorting operations. Special samples include sludges and deposits, grab samples from belts, boiler testing, weather data, and other samples such as mists and stack effluents. The total tests represent the total pieces of data produced by the laboratory. Although it does not exist, in the "typical" or "average" month, the laboratory staff of one chemist and four technicians completed 2812 tests on 493 samples.

From the equipment listed in Table I-B-1, the capital expenses needed to outfit a modest shale oil laboratory, such as the Paraho laboratory, would be about \$75,000 for this major equipment. Expendables plus small items cost another \$25,000. In order to reduce the costs of tests performed by commercial laboratories, an additional \$20,000 would be needed. All of the equipment listed in Table I-B-1 were used routinely. All were



needed; all performed satisfactory (see Table I-B-1 for comments regarding individual pieces of equipment).

The precision of data obtained by most of the "routine" tests was determined by replicate analyses of an oil, raw shale, and retorted shale. These materials were obtained after retorting operations using freshly mined material (about January 1975). The oil was carefully blended and stored in glass pint bottles. The shales were ground to -20 mesh, blended, and stored in sealed 5-gallon cans. Sampling from these storage cans was by riffle-splitting only. The gas standard was a calibrated mixture prepared by Inade Company in a gas cylinder and introduced to the laboratory gas chromatograph by a manifold system. These standards were run about twice a month by the technician doing the test at that time. No special precautions were taken or special preparations made in analyzing these standards. Thus, the data shown in Table I-C-1 represent typical day-to-day precision that could be expected in the analysis of routine samples. The precision does not represent the best that could be achieved.

Because of the absence of well defined standard materials, it is difficult to assess the accuracy of the data obtained by the Paraho laboratory. Throughout the life of the project (and particularly at the start) samples of oil shale products were sent to other laboratories for analysis. Data in Table I-D-1 through 4 show the comparison of results obtained by the Paraho Laboratory and other laboratories for raw shale, retorted shale, oil, and retolene gas. Since, for the most part, the differences in the paired data are less than 2 standard deviations (shown in Table I-C-1), the

Paraho results are not biased. If we assume the other laboratories obtain the true value, the error of the Paraho data is about the same as the precision.

TABLE 1-4-2  
Paraho Laboratory  
Sample Counts

Month - Year	Routine Tests							Special Samples	Total Tests
	TA	Drain	Hot Sales	Hot	Hot	Hot	Hot		
Jan 74		30		10				83	278
Feb 74		7		8				68	258
Mar 74	26	45		45				73	912
Apr 74	26	7		25				65	125
May 74	4	7		4				152	594
Jun 74	27	25		14				145	1001
Jul 74	85	27	25	24	1	10		92	1271
Aug 75	108	15	25	32	12	30		112	2000
Sep 75	152	110	25	113	26	25	25	124	1420
Oct 75	94	170	25	83	11	80	30	160	2026
Nov 75	25	15		21	2	30	105	203	2944
Dec 75	108	112	25	88	44	115	170	199	2753
Jan 76	121	201	25	105	15	103	37	187	4173
Feb 76	86	75	25	154	26	164	62	188	4498
Mar 76	140	180	25	144	23	115	42	318	4640
Apr 76	6	7	25	14	4	79	10	108	1261
May 76	9	85	25	72	44	40	120	204	4108
Jun 76	243	107	25	171	80	135	47	174	2487
Jul 76	157	45	25	108	21	95	101	179	2504
Aug 76	270	140	25	74	50	105	118	198	3033
Sep 76	180	117	25	95	120	70	140	142	3305
Oct 76	145	180	25	100	20	80	70	110	4290
Nov 76	80	45	25	45	12	50	147	186	1878
TOTAL	2004	1207	254	1341	300	1117	1700	3764	44,412





TABLE I-A-1

PARAHO LABORATORY EQUIPMENT

TABLE I-A-1

Paraho Laboratory

Sample Count

Month - Year		Routine Samples							Special Samples	Total Tests
		FA	Shale	Raw Moist.	Oil	Cond.	Gas	CHN		
Jun	74		20		15				83	278
Jul	74		7		6				68	258
Aug	74	26	82		48				73	922
Sep	74	29	2		15				66	525
Oct	74	4	4		5	3	2		110	369
Nov	74	17	21		14		18		115	1021
Dec	74	67	37	15	24	5	25		92	1271
Jan	75	128	95	18	52	12	50		215	2688
Feb	75	152	126	19	113	26	85	19	143	3420
Mar	75	94	109	49	62	12	46	86	202	2828
Apr	75	29	44	7	31	2	38	121	213	2844
May	75	108	112	56	68	44	115	136	184	3703
Jun	75	121	124	58	103	15	105	37	167	4173
Jul	75	86	83	42	154	26	164	51	188	4485
Aug	75	149	144	94	144	23	110	61	158	4643
Sep	75	8	8	9	14	4	19	10	206	1201
Oct	75	9	68	34	72	44	46	119	202	3199
Nov	75	245	207	71	171	80	115	67	171	5657
Dec	75	165	86	35	108	21	50	151	176	3586
Jan	76	178	144	60	76	59	105	110	197	4890
Feb	76	158	171	53	91	125	78	149	349	5305
Mar	76	145	108	29	100	39	94	26	210	4290
Apr	76	86	81	31	45	19	52	147	116	3076
TOTAL	2004		1883	680	1531	559	1317	1290	3704	64,612



TABLE 1-A-1  
Petrochemical Laboratory  
Sample Counts

Month - Year	Routine Samples					Special Samples	Total Tests
	Gas	Cond.	Oil	New Molec.	Spale		
Jan	74		12		30	62	178
Feb	74		4		7	66	328
Mar	74		48		43	77	921
Apr	74		12		2	66	222
May	74		2		4	110	363
Jun	74		14		21	112	1021
Jul	74		24	12	17	92	1271
Aug	74		62	14	62	212	2088
Sep	74		112	12	120	142	1420
Oct	74		62	48	109	202	2828
Nov	74		21	7	44	212	2844
Dec	74		68	26	112	194	3702
Jan	75		102	28	124	162	4172
Feb	75		104	42	62	188	4482
Mar	75		144	64	144	128	4642
Apr	75		14	4	8	206	1201
May	75		72	24	68	202	1192
Jun	75		121	71	207	171	2627
Jul	75		108	32	88	176	2286
Aug	75		76	60	144	192	4880
Sep	75		91	21	111	249	2102
Oct	75		106	29	108	210	4290
Nov	75		42	21	61	116	2026
TOTAL	2608	1882	680	1221	228	3704	84,812

TABLE I-B-1

PARAHO LABORATORY EQUIPMENT

Fischer Assay Bench

Supplier: Electric Power Equipment Company

Cost: \$25000

Comments: The Paraho FA bench represents a marked improvement over the equipment described in U.S.B.M. RI 6676. The biggest improvement is the use of continuous control, L & N, "Electromax III" Controller 6432-3-0056-370-0-20, and proportional heat, L & N "Zero Voltage Power Package" 11906-223. Further improvements could be made by installing the recorder in the control chassis, placing switches on all thermocouples, and replacing the L & N "Trend-trak" with electronic control of the heating curve.

Gas Chromatograph

Supplier: Hewlett-Packard

Cost: \$8600

Comments: The 5712-A GC did analyze components in recycle gas from hydrogen to C-6's but it was not ideal. In order to obtain the maximum information with maximum sensitivity and minimum analytical time, three chromatographs are needed - one for hydrogen; one for "air peak"; and one for the light hydrocarbons with a back flush device for the C-6<sup>+</sup> components.

On-stream Gas Chromatograph

Supplier: Sun Oil Company, AMMD



# TABLE I-B-1

## PARADO LABORATORY EQUIPMENT

Fischer Assay Bench

Supplier: Electric Power Equipment Company

Cost: \$25000

Comments: The Parado FA bench represents a marked improvement over the equipment described in U.S.A.M. RI 6676. The biggest improvement is the use of continuous control, I & N, "Electromax III" Controller 6432-3-0056-370-0-20, and proportional heat, I & N "Zero Voltage Power Package" 11906-223. Further improvements could be made by installing the recorder in the control chassis, placing switches on all thermocouples, and replacing the I & N "Trend-Link" with electronic control of the heating curve.

Gas Chromatograph

Supplier: Hewlett-Packard

Cost: \$8600

Comments: The 571-A GC did analyze components in twelve gas from hydrogen to C-6's but it was not ideal. In order to obtain the maximum information with maximum sensitivity and minimum analytical time, three chromatographs are needed - one for hydrogen; one for "air peak"; and one for the light hydrocarbons with a back flash device for the C-6+ components.

On-stream Gas Chromatograph

Supplier: Sun Oil Company, AND

Cost: \$6700

Comments: More automated, on-stream instrumentation of this kind is needed. The on-stream GC provided useful data for operations control with less than 5% down-time for instrument failure, maintenance, and calibration.

#### Viscosimeters

Supplier: (A) Fisher/Tag

Cost: (B) Precision

Cost: (A) \$750

(B) \$750

Comments: Although the Fischer/Tag instrument has a simple means for setting a new temperature, the Precision provided better temperature control and ease of operation for routine work. Both worked well.

#### Ramsbottom Carbon Furnace

Supplier: Precision

Cost: \$1100

Comments: This instrument, a "left-over" from earlier shale projects, provided adequate data with very little maintenance needed.

#### Centrifuge

Supplier: (A) Precision

(B) Precision

Cost: (A) \$425

(B) \$400



Cost: \$6700

Comments: More automated, on-stream instrumentation of this kind is needed. The on-stream GC provided useful data for operations control with less than 5% down-time for instrument failure, maintenance, and calibration.

### Viscometers

Supplier: (A) Fisher/Tag

(B) Precision

Cost: (A) \$750

(B) \$750

Comments: Although the Fisher/Tag instrument has a simple means for setting a new temperature, the Precision provided better performance control and ease of operation for routine work. Both worked well.

### Hamilton Carbon Furnace

Supplier: Precision

Cost: \$1100

Comments: This instrument, a "last-over" from earlier shale projects, provided adequate data with very little maintenance needed.

### Centrifuge

Supplier: (A) Precision

(B) Precision

Cost: (A) \$425

(B) \$400

Comments: These Centrifuges, used to determine sediment in oils (A) and separate the FA oil-water (B), provided adequate trouble free service.

#### Oven

Supplier: (A) Thelco B  
(B) Napco (1-620-9)  
(C) Precision (1472)

Cost: (A) \$850

(B) \$500

(C) \$400

Comments: These ovens, used to warm oil samples (A and B) and determine shale moisture (C), provided adequate, trouble free service.

#### Furnace

Supplier: Lindberg Hevi-Duty

Cost: \$800

Comments: The furnace, another "left-over", only needed a new set of elements to provide adequate service.

#### Coffeemill Grinder

Supplier: Denver Equipment

Cost: \$1550

Comments: After the addition of skirting to curtail dust losses, this grinder, No. 1 Type D, reduced 1/4" raw shale to -20 mesh quite efficiently.



Comments: These centrifuges, used to determine sediment in oils (A) and separate the PA oil-water (B), provided adequate trouble free service.

Ovens

Supplier: (A) Thermo B  
(B) Napco (1-630-5)  
(C) Precision (1473)  
Cost: (A) \$850  
(B) \$250  
(C) \$400

Comments: These ovens, used to water oil samples (A and B) and determine shale moisture (C), provided adequate, trouble free service.

Furnace

Supplier: Lindberg Heavy-Duty  
Cost: \$600

Comments: The furnace, another "left-over", only needed a new set of elements to provide adequate service.

Colloidal Grinder

Supplier: Denver Equipment  
Cost: \$1250

Comments: After the addition of skirting to curball drum losses, this grinder, No. 1 Type G, reduced 1/4" raw shale to ~30 mesh quite efficiently.

#### Orbital Grinder

Supplier: SPEX "Shatterbox"

Cost: \$2000

Comments: The Model 8500 grinder reduced 3 x 25 gm of shale samples to -100 mesh in a few minutes. No maintenance has been required.

#### Elemental Analyzer

Supplier: Perkin-Elmer Corporation

Cost: \$14000

Comments: The Model 240 analyzer was used to determine total C, H, and N in oils and raw and retorted shales. About 15% of the time is required for maintenance and calibration.

#### Sulfur Analyzer

Supplier: LECO

Cost: \$2900

Comments: The Model 521, loaned to the project, was used to determine total S in oil and raw and retorted shale.

#### Colorimeter

Supplier: Spectronic

Cost: \$600

Comments: The Model 20 was adequate for the needs of this project. A larger instrument, capable of uv detection, should be considered for long-range applications.



Orbital Grinder

Supplier: SPEX "Shatterbox"

Cost: \$2000

Comments: The Model 8200 (grinder reduced 1 x 32 gm of shale samples to -100 mesh in a few minutes. No maintenance has been required.

Elemental Analyzer

Supplier: Perkin-Elmer Corporation

Cost: \$14000

Comments: The Model 340 analyzer was used to determine total C, H, and N in oil and raw and retorted shales. About 15% of the time is required for maintenance and calibration of the instrument.

Sulfur Analyzer

Supplier: LECO

Cost: \$2900

Comments: The Model 521, loaned to the project, was used to determine total S in oil and raw and retorted shales.

Colorimeter

Supplier: Spectronic

Cost: \$800

Comments: The Model 20 was adequate for the needs of this project. A larger instrument, capable of uv detection, should be considered for long-range applications.

TABLE I-C-1  
PARATE LABORATORY  
PRECISION DATA

**Titrimeter**

Supplier: Sargent-Welch

Cost: \$3200

Comments: This Model DG titrimeter is ideally suited to our needs ( $H_2S$  and  $NH_3$  in absorber solutions). Since changing titrants on the model is difficult, another titrimeter would be better suited to a larger laboratory.

**Balances**

Supplier: Mettler

Cost: (A) \$1700

(B) \$1400

(C) \$1150

Comments: These balances, Models P5N, H34, and P203, operated well in the non-ideal laboratory conditions at Anvil Points. The heavy-duty overhead balance, Model P5N, could be replaced readily by an O'Haus triple beam balance costing \$30.



**Titrimeter**

Supplier: Sargent-Welch

Cost: \$1200

Comments: This Model DG titrimer is ideally suited to our needs (H<sub>2</sub> and NH<sub>3</sub> in absorber solutions). Since changing titrants on the model is difficult, another titrimer would be better suited to a larger laboratory.

**Balances**

Supplier: Mettler

Cost: (A) \$1700

(B) \$1400

(C) \$1150

Comments: These balances, Models P2N, H24, and P203, operated well in the non-ideal laboratory conditions at Anvil Pointe. The heavy-duty overhead balance, Model P2N, could be replaced readily by an O'Hara triple beam balance costing \$10.

TABLE I-C-1

PARAHO LABORATORY

Mean

Std. Dev. (1)

C. OIL STANDARD

PRECISION DATA

Water, Wt%	26	0.33	0.07
Sediment, Gg/100 ml	N	Mean	Std. Dev. (1)

A. RAW SHALE STANDARD

Fischer Assay

210°F

Oil Yield, Gal/Ton	45	29.10	0.58
Water Yield, Gal/Ton	45	3.13	0.43
Gas + Loss, Wt%	45	2.29	0.32

Mineral CO <sub>2</sub> , Wt%	20	17.40	0.26
-------------------------------	----	-------	------

Ash, Wt%	20	66.25	0.51
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Moisture, Wt%	20	0.31	0.06
---------------	----	------	------

Hydrogen, Wt%	33	11.17	0.12
---------------	----	-------	------

Elemental	33	2.13	0.23
-----------	----	------	------

Carbon, Wt%	44	17.49	0.14
-------------	----	-------	------

Hydrogen, Wt%	44	1.86	0.08
---------------	----	------	------

Nitrogen, Wt%	44	0.53	0.03
---------------	----	------	------

B. RETORTED SHALE STANDARD

Fischer Assay

Carbon Monoxide

Oil Yield, Gal/Ton

Water Yield, Gal/Ton

Gas + Loss, Wt%

Ethane

Mineral CO<sub>2</sub>, Wt%

Ash, Wt%

Moisture, Wt%

Elemental

Carbon, Wt%	27	6.82	0.16
-------------	----	------	------

Hydrogen, Wt%	27	0.26	0.07
---------------	----	------	------

Nitrogen, Wt%	27	0.25	0.02
---------------	----	------	------

If the measurements are normally distributed, 2/3 of the measurements will be between plus and minus one std. dev. from the mean, and 95% between plus and minus two std. dev.



TABLE I-C-1  
PARADO LABORATORY  
PRECISION DATA

A. RAW SHALE STANDARD			
Fischer Assay			
	N	Mean	Std. Dev. (I)
Oil Yield, Gal/Ton	45	29.10	0.58
Water Yield, Gal/Ton	45	3.13	0.43
Gas + Loss, Wt%	45	2.39	0.32
Mineral CO <sub>2</sub> , Wt%	20	17.40	0.26
Ash, Wt%	20	66.28	0.21
Moisture, Wt%	20	0.31	0.06
Elemental			
Carbon, Wt%	44	17.48	0.14
Hydrogen, Wt%	44	1.86	0.08
Nitrogen, Wt%	44	0.53	0.03
B. RETORTED SHALE STANDARD			
Fischer Assay			
	N	Mean	Std. Dev. (I)
Oil Yield, Gal/Ton	35	0.40	0.16
Water Yield, Gal/Ton	35	0.79	0.25
Gas + Loss, Wt%	35	0.37	0.21
Mineral CO <sub>2</sub> , Wt%	13	16.82	0.40
Ash, Wt%	13	60.10	0.17
Moisture, Wt%	13	0.18	0.06
Elemental			
Carbon, Wt%	27	6.82	0.16
Hydrogen, Wt%	27	0.26	0.07
Nitrogen, Wt%	27	0.25	0.02

TABLE 1-0-1  
Raw Shale Paired Data

	<u>Known</u>	<u>N</u>	<u>Mean</u>	<u>Std. Dev. (1)</u>
--	--------------	----------	-------------	----------------------

C. OIL STANDARD

Water, Wt%	26	0.33	0.07
Sediment, Gm/100 ml	26	1.17	0.20

Viscosity, SUS

130°F	26	156.9	6.0
210°F	26	51.4	2.9

Gravity, °API

Ramsbottom C, Wt%	26	19.3	0.2
	26	2.41	0.28

Elemental

Carbon, Wt%	33	84.53	0.44
-------------	----	-------	------

Hydrogen, Wt%	33	11.17	0.12
---------------	----	-------	------

Nitrogen, Wt%	33	2.13	0.22
---------------	----	------	------

D. GAS STANDARD

GC Analyses, Vol%

Hydrogen	46	15.00	0.43
----------	----	-------	------

Nitrogen	46	26.06	0.63
----------	----	-------	------

Oxygen	46	0.26	0.10
--------	----	------	------

Carbon Monoxide	46	8.00	0.26
-----------------	----	------	------

Methane	46	7.43	0.30
---------	----	------	------

Carbon Dioxide	46	33.16	0.80
----------------	----	-------	------

Ethylene	46	4.03	0.16
----------	----	------	------

Ethane	46	3.43	0.31
--------	----	------	------

Propane	46	2.69	0.26
---------	----	------	------

(1) Standard deviation is a measure of the spread of data.

$$s = \sqrt{\frac{\sum_{i=1}^N (X_i - \bar{X})^2}{N-1}}$$

If the measurements are normally distributed, 2/3 of the measurements will be between plus and minus one std. dev. from the mean, and 95% between plus and minus two std. dev.



C. OIL STANDARD

Known	N	Mean	Std. Dev. (1)
Water, Wt%	26	0.33	0.07
Sediment, Gm/100 ml	26	1.17	0.20
Viscosity, SUS			
130°F	26	126.9	6.0
210°F	26	21.4	2.9
Gravity, API	26	19.3	0.2
Refractive C, Wt%	26	2.41	0.28
Elemental			
Carbon, Wt%	33	84.53	0.44
Hydrogen, Wt%	33	11.17	0.12
Nitrogen, Wt%	33	2.12	0.22

D. GAS STANDARD

Known	N	Mean	Std. Dev. (1)
Hydrogen	46	12.07	0.43
Nitrogen	46	26.04	0.63
Oxygen	46	0.29	0.10
Carbon Monoxide	46	7.76	0.26
Methane	46	6.98	0.30
Carbon Dioxide	46	33.87	0.80
Ethylene	46	4.30	0.16
Ethane	46	3.01	0.31
Propane	46	2.68	0.26

(1) Standard deviation is a measure of the spread of data.

$$s = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}}$$

If the measurements are normally distributed, 2/3 of the measurements will be between plus and minus one std. dev. from the mean, and 95% between plus and minus two std. dev.

TABLE I-D-1

Raw Shale Paired Data

	PARAHO	OTHERS
FA, Oil GPT (1)	24.94	25.35(a)
(2)	17.85	18.25(a), 19.45(b), 18.45(c), 18.95(d)
(2)	58.1	56.8(a), 60.9(b), 56.5(c), 57.9(d)
(2)	12.45	11.9(a), 13.15(b), 12.15(c), 14.2(d)
FA, Water, GPT (1)	3.28	3.47(a)
FA, Oil, Sp Gr (1)	0.913	0.901 (a)
	0.915	0.916 (e)
FA, Gas + Loss, Wt%	2.32	1.98 (a)
Elemental		
Total C, Wt%	17.19	17.33(f), 17.11 (g)
Total H, Wt%	1.85	1.80(f), 1.65(g)
Total N, Wt%	0.53	0.55 (f), 0.53(g)
Total S, Wt%	0.72	0.71 (g)

(1) Mean of ten replicate analyses

(2) Paired data, four random samples from twenty-two

Laboratories: (a) L.E.R.C.  
 (b) CSMRI  
 (c) Core  
 (d) Tosco  
 (e) Hauser  
 (f) Huffman  
 (g) Sun

(1) Five random samples were taken from thirteen.

Laboratories: (a) L.E.R.C.  
 (b) Paraho (PE240)  
 (c) Huffman  
 (d) Sun



TABLE I-D-1

New Spade Patted Data

OTHERS		PARABOL	
PA, Oil CPT (1)	24.94	22.32(a)	
(2)	17.85	18.22(a), 19.42(b), 18.42(c), 18.92(d)	
(3)	26.1	26.8(a), 26.2(b), 26.2(c), 27.2(d)	
(4)	12.42	11.2(a), 12.12(b), 12.12(c), 14.2(d)	
PA, Water, CPT (1)	3.28	3.47(a)	
PA, Oil, Sp Gr (1)	0.913	0.901(a)	
	0.912	0.912(a)	
PA, Gas + Loss, WTS	2.32	1.98(a)	
Elemental			
Total C, WTS	17.19	17.32(f), 17.11(g)	
Total H, WTS	1.82	1.80(f), 1.62(g)	
Total N, WTS	0.23	0.22(f), 0.23(g)	
Total S, WTS	0.72	0.71(g)	
(1) Mean of ten replicate analyses			
(2) Patted data, four random samples from twenty-two			
Laboratories:			
(a) L.E.R.C.			
(b) CERNI			
(c) Core			
(d) Tosco			
(e) Haver			
(f) Hoffman			
(g) Sun			

Table I-D-2

Retorted Shale Paired Data

		<u>PARAHO</u>	<u>OTHERS</u>
FA, Oil, GPT	(1)	None	None (a)
	(1)	None	None (a)
Vis. SUS, 130	(1)	None	None (a)
	(1)	3.8	3.7 (a)
Water, Wt%	(1)	2.4	2.5 (a)
FA, Water, GPT	(1)	1.8	1.0 (a)
Residbottom C, Wt%	(1)	1.4	0.7 (a)
	(1)	1.4	1.2 (a)
Sediment, Mi/100	(1)	1.4	1.2 (a)
Elemental	(1)	1.0	1.4 (a)
Ash, Wt%		79.19	79.27 (b)
Total N, Wt%		79.04	79.02 (b)
Total S, Wt%		79.83	79.75 (b)
Elemental		0.50	0.48 (a)
Total C, Wt%		5.77	5.86 (c), 5.99 (d)
Total H, Wt%		0.13	0.23 (c), 0.14 (d)
Total N, Wt%		0.18	0.15 (c), 0.25 (d)
Total S, Wt%		0.97	0.96 (d)

(1) Five random samples were taken from thirteen.

Laboratories: (a) L.E.R.C.  
 (b) Paraho (PE240)  
 (c) Huffman  
 (d) Sun



Table 1-D-2

Recorded State Pooled Data

OTHERS	PARASHO		
None(a)	None	PA, OIL, CPT (1)	
None(a)	None	(1)	
None(a)	None	(1)	
3.7(a)	1.8	(1)	
2.5(a)	2.4	(1)	
1.0(a)	1.0	PA, Water, CPT (1)	
0.7(a)	1.4	(1)	
1.2(a)	1.4	(1)	
1.2(a)	1.4	(1)	
1.4(a)	1.0	(1)	
79.27(b)	79.19	Ann. Wt%	
79.02(b)	79.04		
79.75(b)	79.83		
		Elemental	
2.86(c), 2.99(d)	2.77	Total C, Wt%	
0.23(c), 0.14(d)	0.13	Total H, Wt%	
0.15(c), 0.25(d)	0.18	Total N, Wt%	
0.96(d)	0.97	Total S, Wt%	

(1) Five random samples were taken from thirteen.

Laboratories: (a) L.E.R.C.

(b) Parasho (P2340)

(c) Hoffman

(d) Sun

TABLE I-D-3  
Oil Paired Data

	PARAHO	
API Gravity, 60°F	19.8	19.5(a), 20(b), 19.5(c)
Hydrogen, Vol%	20.4	20.1(c)
Nitrogen, Vol%	44.3	44(c)
Vis. SUS, 130°F	49.6	50.3(a)
Water, Wt%	0.04	0.1(a)
Pathways, Vol%	1.13	0.80(c)
Ramsbottom C, Wt%	2.49	2.6(b) (1)
Carbon Residue, Vol%	1.97	2.05(c)
Carbon	1.05	0.85(c)
Sediment, ml/100 gm		
Elemental		
Ethylene		
Total C, Wt%	84.93	84.95(d), 85.07(e)
Arthane		
Total H, Wt%	11.36	11.37(d), 10.82(e)
Total N, Wt%	2.24	1.93(d), 2.06(e)
Propane		
Total S, Wt%	0.50	0.48(e)
1-Butane		
Pour Point, °F	85	90(a), 85(b)
n-Butane, Vol%		
1-Pentane, Vol%		
n-Pentane, Vol%		

(1) Ramsbottom C calculated from Conradson C

- Laboratories: (a) Sohio  
(b) P.A.R.C.  
(c) Hauser  
(d) Huffman  
(e) Sun



TABLE 1-2-2  
ANALYTICAL DATA

ANALYST	DATE	CONCENTRATION
Gravel, %	19.8	19.2(a), 20(b), 19.2(c)
Gravel, %	20.4	20.1(c)
Gravel, %	44.1	44(c)
Gravel, %	48.8	50.3(a)
Water, wt	0.04	0.1(a)
Water, wt	1.13	0.80(c)
Remanent C, wt	1.43	2.4(b), (1)
Remanent C, wt	1.97	2.02(c)
Sediment, ml/100 gm	1.02	0.82(c)
Elemental		
Total C, wt	84.82	84.82(a), 82.07(c)
Total H, wt	11.36	11.37(a), 10.82(c)
Total N, wt	2.34	1.92(a), 2.06(c)
Total S, wt	0.20	0.48(a)
Total Point, %	82	90(a), 82(b)

(1) Remanent C calculated from Carbon C

- Laboratory: (a) Soils  
(b) F.A.R.C.  
(c) Husey  
(d) Eutman  
(e) Geo

TABLE I-D-4

Gas Paired Data

	PARAHO	OTHERS
Hydrogen, Vol% (1)	15.00	15.0(a) , 15.18(b)
Nitrogen, Vol% (1)	26.06	25.8(a) , 26.01(b)
(2)	5.33	5.10(b)
Oxygen, Vol% (2)	0.00	0.02(b)
Methane, Vol% (1)	7.43	7.0(a) , 7.91(b)
(2)	71.17	70.48(b)
Carbon Monoxide, Vol% (1)	8.00	7.6(a) , 7.24(b)
Carbon Dioxide, Vol% (1)	33.16	34.3(a) , 32.26(b)
(2)	1.12	1.06(b)
Ethylene, Vol% (1)	4.03	4.0(a) , 3.87(b)
Ethane, Vol% (1)	3.43	3.5(a) , 4.15(b)
(2)	8.83	9.08(b)
Propane, Vol% (1)	2.69	2.6(a) , 2.87(b)
(2)	6.06	5.93(b)
i-Butane, Vol% (2)	2.64	2.95(b)
n-Butane, Vol% (2)	2.69	2.96(b)
i-Pentane, Vol% (2)	1.07	0.96(b)
n- Pentane, Vol% (2)	1.08	0.95(b)
Hydrogen Sulfide, Vol%	0.12	0.16(c)
Ammonia, Vol%	0.10	0.06(c)

(1) Paraho standard cylinder #2

(2) Phillips primary standard

Laboratories: (a) Sun  
 (b) ARCO  
 (c) Gulf



TABLE 1-2-4  
Gas Retention Data

OTHERS	PARAFFINS	
15.0(a), 15.18(b)	15.00	Hydrogen, Vol% (1)
25.8(a), 26.01(b)	26.06	Nitrogen, Vol% (2)
5.10(b)	5.13	Oxygen, Vol% (1)
0.05(b)	0.00	Water, Vol% (1)
7.0(a), 7.91(b)	7.43	Carbon Monoxide, Vol% (1)
70.48(b)	71.17	Carbon Dioxide, Vol% (1)
7.6(a), 7.34(b)	8.00	Ethane, Vol% (1)
14.3(a), 31.26(b)	33.16	Propane, Vol% (1)
1.06(b)	1.12	i-Butane, Vol% (2)
4.0(a), 3.87(b)	4.03	n-Butane, Vol% (2)
3.5(a), 4.15(b)	3.43	i-Pentane, Vol% (2)
9.08(b)	8.83	n-Pentane, Vol% (2)
2.6(a), 2.87(b)	2.69	i-Hexane, Vol% (2)
2.93(b)	2.06	n-Hexane, Vol% (2)
2.95(b)	2.64	i-Heptane, Vol% (2)
2.86(b)	2.69	n-Heptane, Vol% (2)
0.86(b)	1.07	i-Octane, Vol% (2)
0.95(b)	1.08	n-Octane, Vol% (2)
0.16(c)	0.12	Hydrogen Sulfide, Vol%
0.06(c)	0.10	Ammonia, Vol%

(1) Paraffin standard cylinder 12  
(2) Phillips primary standard

Laboratory: (a) Gas  
(b) ASCO  
(c) Gais

**2. LABORATORY  
PROCEDURES**





## II. LABORATORY PROCEDURES

The methods described in this section represent all the methods used by the Paraho laboratory for the analysis of raw and retorted shale, crude shale oil, and recycle and stack gas. These methods represent the final versions of those labeled "TENTATIVE" that were mailed to participants 10/3/74 and discussed at the October 5, 1974 Technical Advisory Committee. No methods for product water, boiler water, or ground and surface water have been included.

Although many of the analytical procedures evolved during the Paraho project, most of the basic methods were obtained from other sources. The shale methods were obtained from the Bureau of Mines (G.L. Cook:RNH: 5/16/74; encl., "Analytical Methods for Oil Shale and Shale Oil"). Most of the oil methods were obtained from ASTM Standards Part 17 "Petroleum Products - Fuels, Solvent, Engine Tests, Lubricating Oils, Cutting Oils, Grease." In addition, several participants gave valuable help and useful suggestions in the development of these final methods. Only the gas chromatography and condensate methods for recycle gas can be considered to be developed in the Paraho laboratory. The method for recycle gas contaminants are taken from EPA methods (Federal Register, 38, 111, June 11, 1973) or ASTM Standards Part 23 "Industrial Water; Atmospheric Analysis."

The methods are divided into four categories: P-P-xx, Laboratory Procedures and Sample Preparation; P-S-xx, Shale Methods; P-O-xx, Oil Methods; P-G-xx, Gas Methods. These methods represent the procedures used in the Paraho laboratory. They are not to be considered standard methods



# II. LABORATORY PROCEDURES

The methods described in this section represent all the methods used by the Petrochemical Laboratory for the analysis of raw and reformed shale, crude shale oil, and recycle and stack gas. These methods represent the final versions of those labeled "TENTATIVE" that were mailed to participants 10/1/54 and discussed at the October 5, 1954 Technical Advisory Committee. No methods for product water, boiler water, or ground and surface water have been included.

Although many of the analytical procedures evolved during the Petrochem project, most of the basic methods were obtained from other sources. The shale methods were obtained from the Bureau of Mines (G.L. Cook:BNM 5/15/54; encl., "Analytical Methods for Oil Shale and Shale Oil"). Most of the oil methods were obtained from ASTM Standards Part 17 "Petroleum Products - Tests, Solvent, Engine Tests, Lubricating Oils, Cutting Oils, Greases". In addition, several participants gave valuable help and useful suggestions in the development of these final methods. Only the gas chromatography and condensate methods for recycle gas can be considered to be developed in the Petrochem Laboratory. The method for recycle gas condensate are taken from EPA methods (Federal Register, 38, 111, June 11, 1973) or ASTM Standards Part 15 "Industrial Water, Atmospheric Analysis".

The methods are divided into four categories: P-P-X, Laboratory Procedures and Sample Preparation; P-S-X, Shale Methods; P-O-X, Oil Methods; P-G-X, Gas Methods. These methods represent the procedures used in the Petrochem Laboratory. They are not to be considered standard methods

for refereeing data disputes.

## OIL SHALE DEMONSTRATION LABORATORY PROCEDURES

### Preparation

Sample Log	P-P-01
Data Handling	P-P-02
Shale Samples - Preparation Scheme	P-P-03
Oil Samples - Preparation Scheme	P-P-04
Gas Samples - Preparation Scheme	P-P-05

### Shale Samples

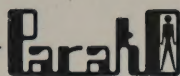
Modified Fischer Assay	P-S-01
Mineral CO <sub>2</sub> (Mineral Carbon)	P-S-02
Moisture	P-S-03
Ash	P-S-04
Total C, H, N	P-S-05
Percent Solubles	P-S-06
Density (Air Pycnometer)	P-S-07
Particle Size Distribution, No-Tap	P-S-08
Free Shale Moisture	P-S-09
Total Sulfur	P-S-10
Free Line	P-S-11

### Oil Samples

API Gravity, 60°	P-O-01
Viscosity, Saybolt, 130°, 210°	P-O-02
Water	P-O-03



for releasing data subject



## PARAHO OIL SHALE DEMONSTRATION

### LABORATORY PROCEDURES

#### Preparation

Sample Log	P-P-01
Data Handling	P-P-02
Shale Samples - Preparation Scheme	P-P-03
Oil Samples - Preparation Scheme	P-P-04
Gas Samples - Preparation Scheme	P-P-05

#### Shale Samples

Modified Fischer Assay	P-S-01
Mineral CO <sub>2</sub> (Mineral Carbon)	P-S-02
Moisture	P-S-03
Ash	P-S-04
Total C, H, N	P-S-05
Benzene Solubles	P-S-06
Density (Air Pycnometer)	P-S-07
Particle Size Distribution, Ro-Tap	P-S-08
Raw Shale Moisture	P-S-09
Total Sulfur	P-S-10
Free Lime	P-S-11

#### Oil Samples

API Gravity, 60°	P-O-01
Viscosity, Saybolt, 130°, 210°	P-O-02
Water	P-O-03



LABORATORY PROCEDURES

PREPARATION

P-1-01	Sample log
P-1-02	Core handling
P-1-03	Shale Samples - Preparation Scheme
P-1-04	Oil Samples - Preparation Scheme
P-1-05	Gas Samples - Preparation Scheme

Shale Samples

P-2-01	Modified Fischer Assay
P-2-02	Mineral CO <sub>2</sub> (Mineral Carbon)
P-2-03	Moisture
P-2-04	Ash
P-2-05	Total C, H, N
P-2-06	Benzene Solubles
P-2-07	Density (Air Pycnometer)
P-2-08	Particle Size Distribution, No. 75
P-2-09	Raw Shale Moisture
P-2-10	Total Sulfur
P-2-11	Free Lime

Oil Samples

P-3-01	API Gravity, 60°
P-3-02	Viscosity, Saybolt, 150°, 210°
P-3-03	Water

Ramsbottom Carbon	P-O-04
Sediment	P-O-05
Total C, H, N	P-O-06
Atmospheric Distillation	P-O-07
Pour Point	P-O-08
Ash	P-O-09
Pycnometer Gravity	P-O-10
Total Sulfur	P-O-11

#### Gas Samples

GC Procedure	P-G-01
Condensate, Ambient	P-G-02
Condensate, Sub-Ambient	P-G-03
Environmental ( $H_2S$ , $SO_2$ , $NH_3$ , $NO_x$ )	P-G-04
Mist Characterization	P-G-05
On-stream Gas Chromatograph	P-G-06



7-0-04 Resubmission Carbon  
 7-0-05 Sediment  
 7-0-06 Total C, H, N  
 7-0-07 Atmospheric Distillation  
 7-0-08 Pour Point  
 7-0-09 Ash  
 7-0-10 Pyrometric Gravity  
 7-0-11 Total Sulfur

Gas Samples

7-0-01 GC Procedure  
 7-0-02 Condensate, Ambient  
 7-0-03 Condensate, Sub-Ambient  
 7-0-04 Environmental ( $H_2S$ ,  $SO_2$ ,  $NH_3$ ,  $NO_x$ )  
 7-0-05 Heat Characterization  
 7-0-06 On-stream Gas Chromatograph

# PARAHO OIL SHALE DEMONSTRATION

## Log-In Procedure

### Method P-P-01

1. Samples should be logged in the log book upon receipt.
2. No analysis should be done on any sample that is not properly logged in.
3. Sample identification should include the type of sample, the time and date that it was taken, the run, and the sample number.
4. Unless specified, only routine tests will be run. These are:

<u>Raw Shale</u>	<u>Spent Shale</u>	<u>Oil</u>	<u>Gas</u>
Fischer	Fischer	API Grav.	GC
Min. CO <sub>2</sub>	Min. CO <sub>2</sub>	Vis. 130/210	Condensate
Moisture	Moisture	Water	
Ash	Ash	Sediment	
	Total C,H,N	Ramsbottom C	

5. Other tests, such as benzene-solubles, ash (oil) pour point, and distillation, will only be run when requested.



# BARRETT OIL SHALE DEMONSTRATION

## Log-In Procedure

### Method P-P-01

1. Samples should be logged in the log book upon receipt.
2. No analysis should be done on any sample that is not properly logged in.
3. Sample identification should include the type of sample, the time and date that it was taken, the run, and the sample number.
4. Unless specified, only routine tests will be run. These are:

Gas	Oil	Spent Shale	Raw Shale
GC	API Grav.	Fischer	Fischer
Condensate	Vla. 130/310	Min. CO <sub>2</sub>	Min. CO <sub>2</sub>
	Water	Moisture	Moisture
	Sediment	Ash	Ash
	Permselective C	Total C,H,N	

5. Other tests, such as benzene-solubles, ash (all) pour point, and distillation, will only be run when requested.





PARADO OIL SHALE DEMONSTRATION

Data Handling

Method P-P-03

1. All important data should be recorded directly in a bound laboratory notebook. This data includes any numbers needed to identify a sample or perform calculations leading to the reported data.
2. Observations, other than data, should also be entered in the notebook, and, whenever practical, under "Comments" on the reported data sheets (Sheets P-P-1 and P-P-2).
3. Data should be reported as soon as calculations are finished.
4. Data should be reported on the standard sheets (P-P-1 and P-P-2) and a carbon copy retained for the laboratory file. Only one type of sample should be reported on a standard sheet.

PARAHO PROJECT  
CONTROL LABORATORY  
Analytical Report Sheet

Operation Number - \_\_\_\_\_

Date Received \_\_\_\_\_

Submitted by -

Date Reported

### Sample Description

Analyze for

### Method of Analysis

[illegible]

**Comments:**

Reported by: \_\_\_\_\_

P-L-1







PARAHO OIL SHALE DEMONSTRATION

Shale Sample Preparation Scheme

PARAHO PROJECT

FISCHER ASSAY REPORTS

Sample Description	Type						
	Date						
	Time						
	Run No.						
	Sample No.						
Analytical Data	Oil, Wt%						
	Water, Wt%						
	Loss & Gas, Wt%						
	Coking Tendency						
	Oil, Sp. Gr.						
	60/60F						
	Oil, GPT						
Water, GPT							

Comments:

PROCEDURE:

1. If mesh size is  $\frac{1}{4}$  inch, hand screen and grind the oversize material to  $\frac{1}{4}$  inch mesh using the jaw crusher.

2. Weigh sample; if greater than 830 gm, proceed with Sample Preparation - Step I; if 360-825 gm, proceed with Sample Preparation - Step II. Note: If sample is less than 360 gm, use 360 gm sample for Fischer

Analyzed by: \_\_\_\_\_  
Date: \_\_\_\_\_ Checked by: \_\_\_\_\_

3. The excess sample is retained as received in a paper sack for one week. An extra Fischer sample is retained for at least six months.

P-L-2



FISCHER ASSAY REPORTS  
PARADO PROJECT

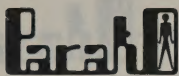
Type	Date	Time	Run No.	Sample No.	Notes
Oil, Wt					
Water, Wt					
Loss & Gas, Wt					
Calcd Tangency					
Oil, Sp. Gr.					
Oil, API					
Water, API					

Comments:

Analysed by: \_\_\_\_\_

Date: \_\_\_\_\_

Checked by: \_\_\_\_\_



## PARAHO OIL SHALE DEMONSTRATION

### Shale Samples Preparation Scheme

#### Method P-P-03

#### SCOPE:

This scheme is designed to prepare two representative samples (-20 mesh, 90-110 gms) for Fischer assay and one sample (-100 mesh, 22-28 gms) for other tests.

#### PROCEDURE:

Depending upon the mesh size and amounts of the incoming sample, 2-3 grinding operations and 5-13 splitting operations are required. For the most part, samples are not split more than four times in succession without one grinding operation. Procedures are designed to provide representative samples for analyses.

#### EQUIPMENT:

Hand screen (1/4 inch)  
Jaw crusher  
Coffee Mill Crusher  
Shatterbox, SPEX  
Riffle Splitters 1/2", 1/4"  
Tyler Screens

#### PROCEDURE:

1. If mesh size is +1/4 inch, hand screen and grind the oversize material to -1/4 inch mesh using the jaw crusher.
2. Weigh sample; if greater than 830 gm, proceed with Sample Preparation - Step I; if 360-825 gm, proceed with Sample Preparation - Step II. Note: If sample is less than 360 gm attempt to obtain two 100-gm samples for Fischer and resid for other tests; notify supervisor.
3. The excess sample is retained as received in a paper sack for one week. An extra Fischer sample is retained for at least six months.



PANAMA OIL SHALE DEMONSTRATION  
Shale Samples Preparation Scheme

Method P-7-03

SCOPE:

This scheme is designed to prepare two representative samples (1-20 mesh, 90-110 gms) for Fischer assay and one sample (1-100 mesh, 25-28 gms) for other tests.

PROCEDURE:

Depending upon the mesh size and amount of the incoming sample, 2-3 grinding operations and 2-13 splitting operations are required. For the most part, samples are not split more than four times in succession without one grinding operation. Procedures are designed to provide representative samples for analysis.

EQUIPMENT:

Hand screen (1/4 inch)  
Jaw crusher  
Coffee Mill Crusher  
Shatterbox, 2500  
Riffle Splitter 1/2, 1/4  
Tyler Screens

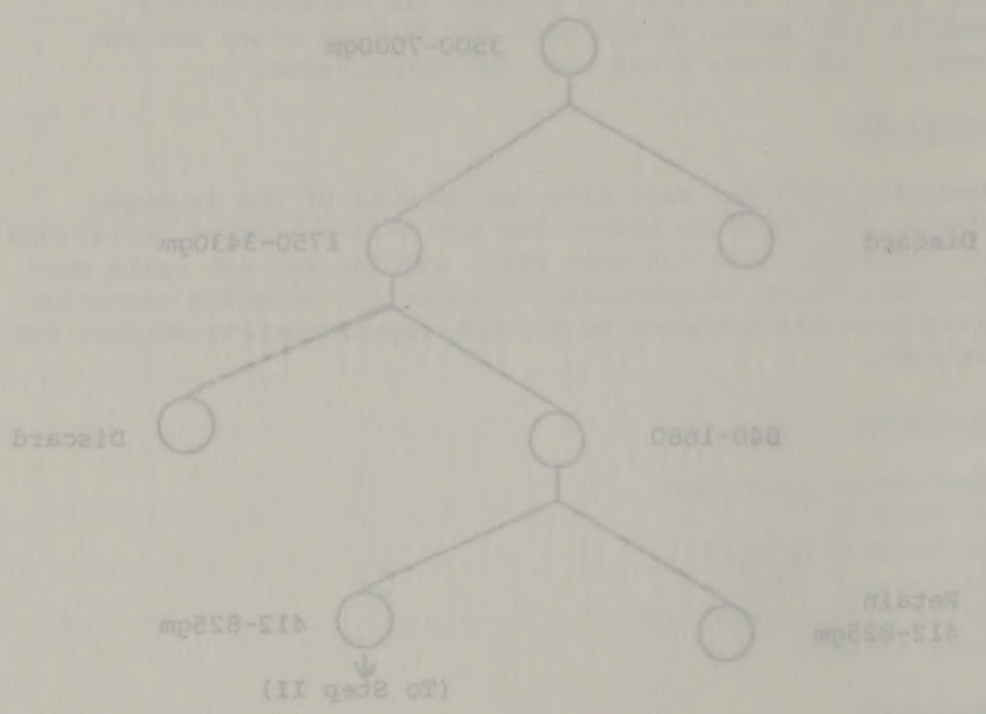
PROCEDURE:

1. If mesh size is 4/ inch, hand screen and grind the oversize material to 1/4 inch mesh using the jaw crusher.
2. Weigh sample, if greater than 820 gm, proceed with Sample Preparation - Step I; if 160-820 gm, proceed with Sample Preparation - Step II. Note: If sample is less than 160 gm attempt to obtain two 100-gm samples for Fischer and tests for other tests; notify supervisor.
3. The excess sample is retained as received in a paper sack for one week. An extra Fischer sample is retained for at least six months.





# SAMPLE PREPARATION - Step I



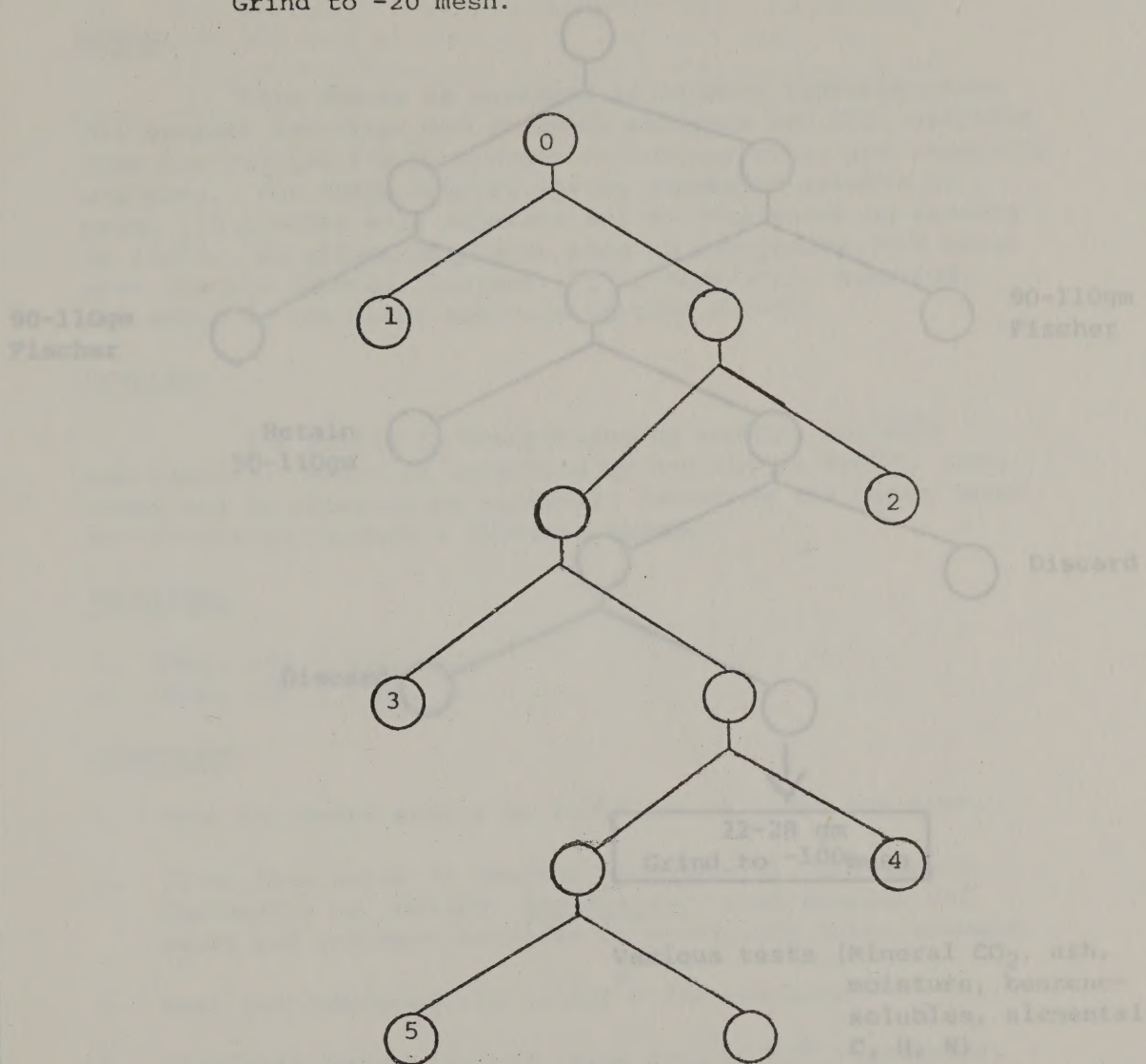
NOTE: If mesh size is  $\frac{1}{4}$  inch, hand sieve and grind oversize material to  $\frac{1}{4}$  inch.

SAMPLE PREPARATION - Step II

(From Step I - 380 to 440 gm)

SAMPLE PREPARATION - Step II

Grind to -20 mesh.



Original wt. (Step II-0)

Fractions retained for Step III

380-440  
445-520  
525-625  
630-745  
750-875

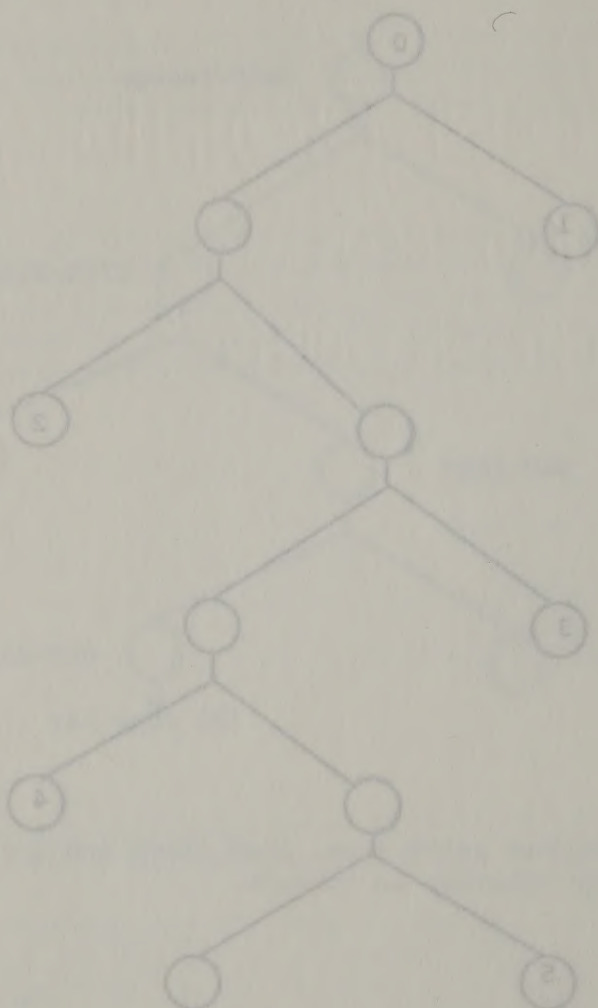
0  
1, 2, 3  
1, 3, 4, 5  
1, 3  
1, 5

\*If no sample was retained from Step I, the unused fractions should be combined and retained.



# SAMPLE PREPARATION - Step II

Grind to -20 mesh.



Fractions retained for Step III

Original wt. (Step II-0)

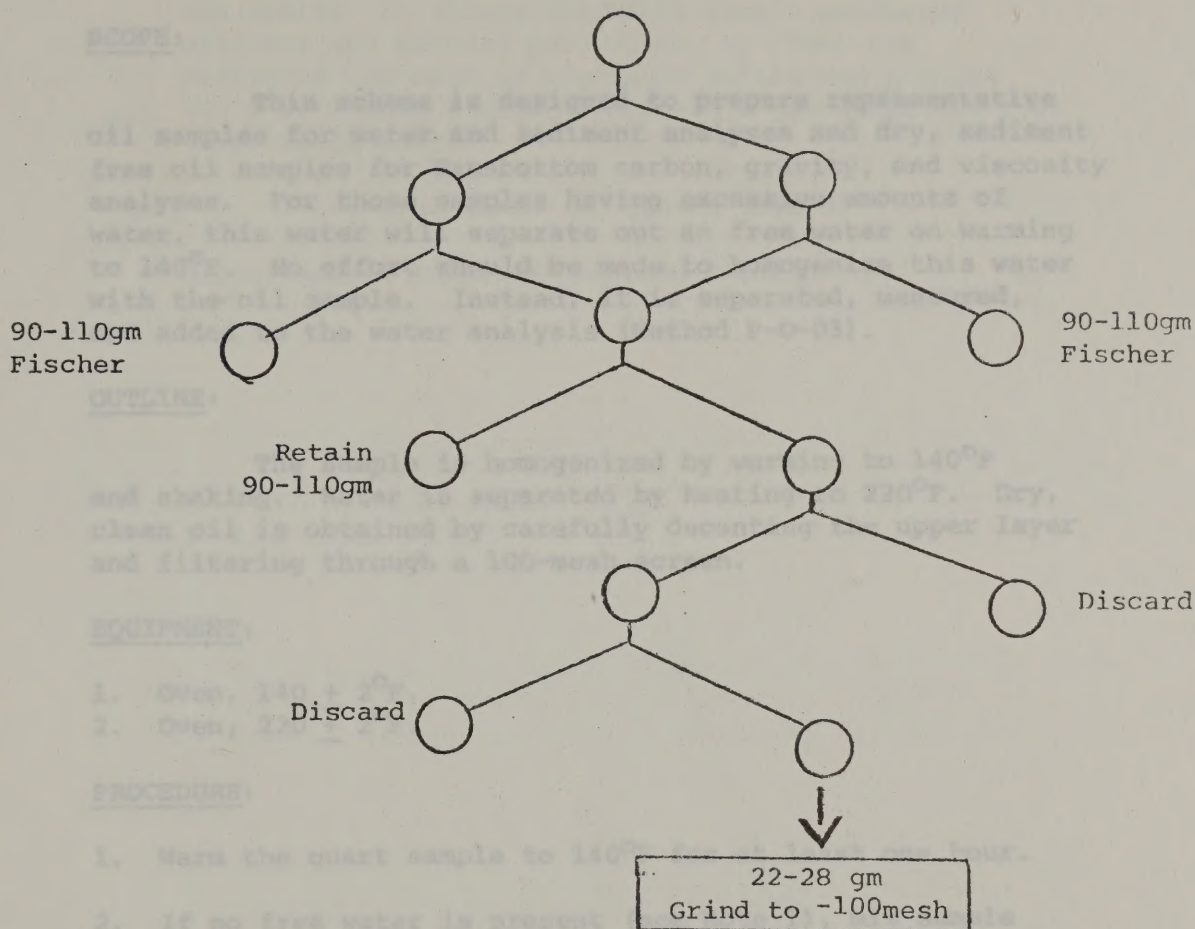
0  
1, 2, 3  
1, 2, 4, 5  
1, 3  
1, 5

380-440  
445-520  
525-625  
630-745  
750-875

\*If no sample was retained from Step I, the unused fractions should be combined and retained.

# SAMPLE PREPARATION - Step III

(From Step II - 380 to 440 gm)



## EQUIPMENT:

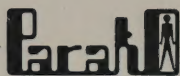
1. Oven, 140° F.
2. Oven, 220° F.

## PROCEDURE:

1. Warm the quart sample to 140° F. for one hour.
  2. If no free water is present, thoroughly by shaking, immediately, take samples for water and sediment analyses in previously labeled vessels.
  3. Heat the remaining oil to 220° F. for one hour.
  4. Carefully decant the oil layer into a 100° mesh filter, passing the oil through a 100-mesh filter. Set the quart bottle aside.
  5. From the filtered, dry oil, remove a sample for flashpoint carbon.
  6. Carefully decant the oil remaining in the quart bottle into a 100° viscometer, passing the oil through a 100-mesh filter.
  7. Use the remainder of the oil for API Gravity.
- Various tests (Mineral CO<sub>2</sub>, ash, moisture, benzene-solubles, elemental C, H, N)







## PARAHO OIL SHALE DEMONSTRATION

### Oil Samples - Preparation Scheme

#### Method P-P-04

##### SCOPE:

This scheme is designed to prepare representative oil samples for water and sediment analyses and dry, sediment free oil samples for Ramsbottom carbon, gravity, and viscosity analyses. For those samples having excessive amounts of water, this water will separate out as free water on warming to 140°F. No effort should be made to homogenize this water with the oil sample. Instead, it is separated, measured, and added to the water analysis (Method P-O-03).

##### OUTLINE:

The sample is homogenized by warming to 140°F and shaking. Water is separated by heating to 220°F. Dry, clean oil is obtained by carefully decanting the upper layer and filtering through a 100-mesh screen.

##### EQUIPMENT:

1. Oven, 140  $\pm$  2°F.
2. Oven, 220  $\pm$  2°F.

##### PROCEDURE:

1. Warm the quart sample to 140°F for at least one hour.
2. If no free water is present (see Note 1), mix sample thoroughly by shaking; immediately, take samples for water and sediment analyses in previously tared vessels.
3. Heat the remaining oil to 220°F for one hour.
4. Carefully decant the oil layer into a 210° viscometer, passing the oil through a 100-mesh filter. Set the quart bottle aside.
5. From the filtered, dry oil, remove a sample for Ramsbottom carbon.
6. Carefully decant the oil remaining in the quart bottle into a 130° viscometer, passing the oil through a 100-mesh filter.
7. Use the remainder of the oil for API Gravity.



# PARAFFIN OIL SHALE DEMONSTRATION

## Oil Samples - Preparation Scheme

Method T-7-54

### SCOPE:

This scheme is designed to prepare representative oil samples for water and sediment analyses and dry, sediment free oil samples for kinematic carbon, gravity, and viscosity analyses. For those samples having excessive amounts of water, this water will separate out as free water on warming to 140°F. No effort should be made to homogenize this water with the oil sample. Instead, it is separated, measured, and added to the water analysis (Method T-C-01).

### OUTLINE:

The sample is homogenized by warming to 140°F and shaking. Water is separated by heating to 230°F. Dry, clean oil is obtained by carefully decanting the upper layer and filtering through a 100-mesh screen.

### EQUIPMENT:

1. Oven, 140 ± 2°F.
2. Oven, 230 ± 2°F.

### PROCEDURE:

1. Warm the quart sample to 140°F for at least one hour.
2. If no free water is present (see Note 1), mix sample thoroughly by shaking; immediately take samples for water and sediment analyses in previously labeled vessels.
3. Heat the remaining oil to 230°F for one hour.
4. Carefully decant the oil layer into a 310° viscometer, passing the oil through a 100-mesh filter. Set the quart bottle aside.
5. From the filtered, dry oil, remove a sample for kinematic carbon.
6. Carefully decant the oil remaining in the quart bottle into a 310° viscometer, passing the oil through a 100-mesh filter.
7. Use the remainder of the oil for API Gravity.

# PARAHO OIL SHALE DEMONSTRATION

Note: If free water is present, obtain the total weight, T, (oil, water, and bottle). Pour the entire content of the bottle into a 1-liter separatory funnel and reweigh the bottle, B. Drain the water into a graduated cylinder and measure the volume, V. Pour the separated oil back to the quart bottle and proceed again with Step 1 under PROCEDURE. Calculate the free water as follows:

## SCOPE:

This procedure is designed primarily to measure the product gas and  $\% \text{ free water} = 100\% \times V/(T-B)$ . Individual gases analyzed are:  $H_2$ ,  $O_2$ ,  $H_2O$ ,  $CO$ ,  $CH_4$ ,  $CO_2$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$ . Report under "Comments" on Form P-L-1.  $SO_2$ ,  $NO_x$ ,  $H_2S$ , and  $Amg$  will be collected and analyzed on an individual basis.

## OUTLINE:

Product gas is cycled from the slower discharge to the control room where it is cleaned and dried by passing through a condenser to a clean 500-ml glass sample bomb. The condensate is taken in a clean glass quart bottle.

## EQUIPMENT:

1. One sample bomb, glass, 500-ml, with stopcock on each end.
2. Bottles, glass, quart, with screw cap closure.

## PROCEDURE:

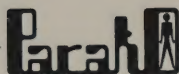
1. Samples should be analyzed as soon as possible after receipt. Storage should be avoided.
2. Analyzed bomb should be flushed with deionized water, dried, then stored ready for a new sample.
3. If the bomb does not drain uniformly after flushing with water, they should be rinsed with deionized solution (acetone, "Alconox," or "Chromerge") then rinsed thoroughly with deionized water.
4. All sample bombs should be cleaned (Step 3) at the end of each retorting operation.
5. After the quart bottle is emptied, it should be cleaned for reuse.



Notes: If free water is present, obtain the total weight,  $T$ , (oil, water, and bottle). Pour the entire content of the bottle into a 1-liter separatory funnel and reweigh the bottle. Drain the water into a graduated cylinder and measure the volume,  $V$ . Pour the separated oil back to the quart bottle and proceed again with Step I under PROCEDURE. Calculate the free water as follows:

$$\% \text{ free water} = 100 \times V / (T - B)$$

Report under "Comments" on Form F-1-1.



## PARAHO OIL SHALE DEMONSTRATION

### Gas Samples - Preparation Scheme

Method P-P-05

#### SCOPE:

This procedure is designed primarily to prepare a product gas sample for gas chromatographic analysis. Individual gases analyzed are:  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO$ ,  $CH_4$ ,  $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$ , and C-3's through C-6's. Other gases, such as  $SO_2$ ,  $NO_x$ ,  $H_2S$ , and  $NH_3$  will be collected and analyzed on an individual basis.

#### OUTLINE:

Product gas is cycled from the blower discharge to the control room where it is cleaned and dried by passing through a condenser to a clean 500-ml glass sample bomb. The condensate is taken in a clean glass quart bottle.

#### EQUIPMENT:

1. Gas sample bombs, glass, 500-ml, with stopcock on each end.
2. Bottles, glass, quarts, with screw cap closure.

#### PROCEDURE:

1. Samples should be analyzed as soon as possible after receipt. Storage should be avoided.
2. Analyzed bombs should be flushed with deionized water, dried, then stored ready for a new sample.
3. If the bombs do not drain uniformly after flushing with water, they should be rinsed with cleaning solution (acetone, "Alconox," or "Chromerge") then rinsed thoroughly with deionized water.
4. All sample bombs should be cleaned (Step 3) at the end of each retorting operation.
5. After the quart bottle is emptied, it should be cleaned for reuse.



# PARAFFIN OIL SHALE CONCENTRATION

## Gas Samples - Preparation Scheme

Method 1-1-52

### SCOPE:

This procedure is designed primarily to prepare a product gas sample for gas chromatographic analysis. Individual gases analyzed are:  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO$ ,  $CH_4$ ,  $CO_2$ ,  $C_2H_6$ , and  $C_3H_8$  through C-6's. Other gases, such as  $SO_2$ ,  $NO_2$ ,  $H_2S$ , and  $NH_3$  will be collected and analyzed on an individual basis.

### OUTLINE:

Product gas is cycled from the blower discharge to the control room where it is cleaned and dried by passing through a condenser to a clean 500-ml glass sample bomb. The condensate is taken in a clean glass quart bottle.

### EQUIPMENT:

1. Gas sample bomb, glass, 500-ml, with stopcock on each end.
2. Bottles, glass, quart with screw cap closure.

### PROCEDURE:

1. Samples should be analyzed as soon as possible after receipt. Storage should be avoided.
2. Analyzed bombs should be flushed with deionized water, dried, then stored ready for a new sample.
3. If the bombs do not drain uniformly after flushing with water, they should be rinsed with cleaning solution (acetone, "Alconox," or "Chromoxene") then rinsed thoroughly with deionized water.
4. All sample bombs should be cleaned (Step 3) at the end of each testing operation.
5. After the quart bottle is emptied, it should be cleaned for reuse.

## PARAHO OIL SHALE DEMONSTRATION

### MODIFIED FISCHER ASSAY

#### Method P-S-01

#### SCOPE:

This method is essentially the Automated Modified Fischer Assay described in detail in the U.S. Department of Interior, Bureau of Mines, RI6676. Principle modifications are in the use of improved programmers, heaters, and thermocouples. The method is applicable to raw and spent shale samples.

#### OUTLINE:

A representative, 100-gm portion of -20 mesh shale is obtained by Method P-P-03. The sample is retorted according to RI6676. Data obtained from the assay are: oil yield, wt% and Gal/Ton; water yield, wt% and Gal/Ton; sp. Gr. (60/60°F)/gas + loss, wt%; coking tendency.

#### APPARATUS:

1. Fischer Assay Apparatus. A 12 unit apparatus has been designed and constructed by Electric Power Equipment Company, 5151 E. 56th Avenue, Commerce City, Colorado 80022.
  - a. Heater case. Transite 3/8", fabricated according to Figure 2, USBM R.I. 6676.
  - b. Heating elements. Ring, 500 watt, 120 volt, Chromalox A20. Tubular, 1045 watt, 120 volt, Chromalox TRI-5212. E & M Sales, 2660 Walnut Street, Denver, CO 80205. Ring heater is separated from bottom by a circle of 1/8" asbestos pad; tubular heater is bent to surround the retort and separated from the sides by about 1/4".
  - c. Thermocouples. Thermo Electric J316-U304-BAY-2-2 5/8"-OP; jack no. 41401. Ross Equipment Company, 2149 S. Clermont, Denver, Colorado 80222.
2. Controller. A controller unit to control and monitor the temperature of the twelve retorts in the Fischer Assay apparatus has been designed and constructed by Electric Power Equipment Company.
  - a. Programmer. "Trendtrak," cat. no. 200-202-099-0056-6-002. Leeds and Northrup, 2715 S. Locust Street, Denver, CO 80222.
  - b. Power Supply. "Zero Voltage Power Package," cat. no. 11906-223. Leeds & Northrup.
  - c. Controller. "Electromax III," model CAT, cat. no. 6432-3-0056-370-0-20. Leeds & Northrup.



# PARADOX OIL SHALE DEMONSTRATION

## MODIFIED FISCHER ASSAY

Method P-2-01

### SCOPE:

This method is essentially the Automated Modified Fischer Assay described in detail in the U.S. Department of Interior, Bureau of Mines, Report. Principal modifications are in the use of improved programming, heaters, and thermocouples. The method is applicable to raw and spent shale samples.

### OUTLINE:

A representative, 100-gr portion of -20 mesh shale is obtained by Method P-2-01. The sample is retested according to Method P-2-01. Data obtained from the assay are: oil yield, wt% and Gal/Ton; water yield, wt% and Gal/Ton; sp. Gr. (60/60°F) gas + loss, wt%; coking tendency.

### APPARATUS:

1. Fischer Assay Apparatus. A 12 unit apparatus has been designed and constructed by Electric Power Equipment Company, 3121 E. 56th Avenue, Commerce City, Colorado 80022.

- Heater case. Transite 3/8", fabricated according to Figure 2, USNM R.I. 5876.
- Heating elements. Ring, 500 watt, 120 volt, Chromalox A30. Tubular, 1045 watt, 120 volt, Chromalox TRI-5212. E & H Heater, 2660 Walnut Street, Denver, CO 80202.
- Ring heater is separated from bottom by a circle of 1/8" asbestos pad. Tubular heater is bent to surround the reactor and separated from the sides by about 1/4".
- Thermocouples. Thermo Electric 3316-U304-2-2 5/8" CP; Jack no. 41401. Ross Equipment Company, 3142 S. Clermont, Denver, Colorado 80222.

2. Controller. A controller unit to control and monitor the temperature of the two reactors in the Fischer Assay apparatus has been designed and constructed by Electric Power Equipment Company.

- Programmer. "Transitak", cat. no. 200-202-093-0056-8-002. Leads and wiring. 3121 E. 56th Street, Denver, CO 80222.
- Power supply. "Zero Voltage Power Package", cat. no. 11204-213. Leads & wiring.
- Controller. "Electroman III", model CAT, cat. no. 4433-3-0056-370-0-10. Leads & wiring.

3. Refrigerated Bath. 10 cu. ft. deep freezer with metal liner filled with 30-40 gallons of 1:1 glycol: water.
4. Centrifuge. Precision Scientific, Model 67310, max. RPM 2200.
5. Balances.
  - a. Mettler P5N, 5000 gm capacity, 0.1 gm readability
  - b. Mettler P203N, 200 gm capacity, 0.01 gm readability
6. Individual components
  - a. Retort #2266, #108 Al Alloy
  - b. Plug #2266A, #108 Al Alloy  
Casting: McPherson Corp., 2027 W. Colfax Ave., Denver, CO 80204  
Machining: McAfee Mach. & Die, 1790 Argonne St., Denver, CO 80111
  - c. Adapter, "Y", Rocky Mountain Glassblowing, 2520 Galena St. Aurora, CO 80010
  - d. Receiver. 100-ml centrifuge tube ASTM D-1796
  - e. Condenser. Allihn, 300 mm., 24/40  $\text{F}$ , drip tip
  - f. Vent Tube + 4 Discs. McAfee Mach. & Die, machined according to Figure 9, U.S.B.M. R.I. 6676
  - g. Drying Tube. Straight form, polyethylene, 200 mm, filled with drying agent and fitted with 3/8" rubber hose.



3. Refrigerated Bath. 10 cu. ft. deep freezer with metal liner filled with 20-40 gallons of 1:1 glycol: water.

4. Centrifuge. Precision Scientific, Model 67310, max. RPM 3200.

5. Balances.

a. Mettler PM, 5000 gm capacity, 0.1 gm readability  
b. Mettler PM20M, 200 gm capacity, 0.01 gm readability

6. Individual components

a. Refract #3265, #108 Al Alloy

b. Ring #3265A, #108 Al Alloy

Castings: McPherson Corp., 2021 W. Colfax Ave., Denver, CO 80204  
Machining: McAfee Mach. & Die, 1790 Argonne St., Denver, CO 80111

c. Adapter, "Y", Rocky Mountain Glassblowing, 2530 Galena St. Aurora, CO 80010

d. Receiver. 100-oz centrifuge tube ASTM D-1395

e. Condenser. Allihn, 300 mm., 24/40 E, drip tip

f. Vent Tube + 4 Discs. McAfee Mach. & Die, machined according to Figure 9, U.S.P. Pat. 2,873,673

g. Drying Tube. Straight form, polyethylene, 200 mm, filled with drying agent and fitted with 3/8" rubber hose.

PROCEDURE:

1. Record all data on "FISCHER ASSAY SHEET" (P-L-3)
2. Weigh an empty retort, four discs, vent tube, plug and stopper to nearest 0.1 gm. All materials should be at room temperature before weighing.
3. Use the entire 90-110 gm portion of "-20 mesh" shale obtained in the preparation of shale samples (P-P-03).
4. Carefully pour the sample into the retort in five layers separated by the four discs. Do not pour any sample into the vent tube.
5. Tap the plug into place and reweigh the entire filled retort to the nearest 0.1 gm.
6. Weigh a clean, dry centrifuge tube and adapter to the nearest 0.01 gm.
7. Assemble the apparatus as shown in Figure 2-1 Immerse the receiver in ice water. Start coolant flowing through the condenser. Turn on the gas vent blower.
8. Turn on the power switch and timer. Observe the apparatus during the automated heating cycle to check for obvious leaks. If leaks occur, note it on P-L-3 and turn off affected retort.
9. After about an hour-and-a-quarter (the timer has shut off the heat), turn off the power switch, timer, and vent blower, stop the coolant flow, and disassemble the apparatus.
10. Attach a drying tube to the retort and allow the retort and the receiver and adapter to come to room temperature.
11. Weigh the distillate, receiver and adapter to the nearest 0.01 gm.
12. Separate the receiver and adapter; place the receiver and distillate in a warm (about 140°F) bath for 10-15 minutes.
13. Clean and dry the condenser and adapter.
14. Centrifuge the receiver and distillate at 2000 rpm for ten minutes.
15. Read the volume of water to the nearest 0.05 ml (if possible). If the interface is indistinct, scrape the inside of the tube with a small wire, reheat, and repeat steps 14 and 15.



PROCEDURE:

1. Record all data on "VISCER ASSEMBLY SHEET" (P-1-3)
2. Weigh an empty retort, four discs, vent tube, plug and stopper to nearest 0.1 gm. All materials should be at room temperature before weighing.
3. Use the entire 90-110 gm portion of "20 mesh" shale obtained in the preparation of shale samples (P-2-03).
4. Carefully pour the sample into the retort in five layers separated by the four discs. Do not pour any sample into the vent tube.
5. Tap the plug into place and reweigh the entire filled retort to the nearest 0.1 gm.
6. Weigh a clean, dry centrifuge tube and adapter to the nearest 0.01 gm.
7. Assemble the apparatus as shown in Figure 2-1. Immerse the receiver in ice water. Start coolant flowing through the condenser. Turn on the gas vent blower.
8. Turn on the power switch and timer. Observe the apparatus during the automated heating cycle to check for obvious leaks. If leaks occur, note it on P-1-3 and turn off affected retort.
9. After about an hour-and-a-quarter (the timer has shut off the heat), turn off the power switch, timer, and vent blower, stop the coolant flow, and disassemble the apparatus.
10. Attach a drying tube to the retort and allow the retort and the receiver and adapter to come to room temperature.
11. Weigh the distillate, receiver and adapter to the nearest 0.01 gm.
12. Separate the receiver and adapter; place the receiver and distillate in a water (about 140°F) bath for 10-15 minutes.
13. Clean and dry the condenser and adapter.
14. Centrifuge the receiver and distillate at 2000 rpm for ten minutes.
15. Read the volume of water to the nearest 0.02 ml (if possible). If the interface is indistinct, scrape the inside of the tube with a small wire, repeat, and repeat steps 14 and 15.

16. Clean up the receiver, for next assay.
17. Remove the drying tube from the retort, and weigh the entire retort (retort, discs, tube, plug and stopper and spent shale) to the nearest 0.1 gm.
18. Disassemble the retort, remove spent shale, and note the coking tendencies (see below)

<u>Condition of Shale</u>	<u>Coking Tendency</u>
Pours easily from retort; no conglomeration noted	None (N)
Required a spatula for complete removal of shale from the retort	Slight (S)
Partially fused, difficult to remove shale from the retort	Moderate (M)
Completely fused, very difficult to remove shale from the retort	Heavy (H)

19. Clean up retort, discs, tube and plug for the next assay.

#### CALCULATIONS:

All calculations are performed on the Fischer Assay Sheet (P-L-3). Instructions are defined on the sheet.

NOTE 1: Since the time consuming specific gravity determination usually produces a repeatable value, a specific gravity of 0.915 may be assumed. Determination of oil yield, gal/ton then simplifies to  $2.619 \times \text{oil yield, wt\%}$ . The specific gravity determination (as described in P-O-10) should be done periodically.

Report on the Fischer Assay Report (P-L-2) the following:

Sample description: "raw" or "spent"  
Date of sample: month/date/year  
Time of sample: military time  
Retort run number, sample number

NOTE: the above information should appear on the sample tag.

Oil, wt% to nearest 0.01 wt%  
Water, wt% to nearest 0.01 wt%  
Loss + Gas to nearest 0.01 wt%  
Coking Tendency: "none," "slight," "moderate," or "heavy."  
Oil, Gal/Ton to nearest 0.1 GPT  
Water, Gal/Ton to nearest 0.1 GPT



16. Clean up the receiver, for next assay.
17. Remove the drying tube from the retort, and weigh the entire retort (retort, glass, tube, plug and stopper and spent shale) to the nearest 0.1 gm.
18. Disassemble the retort, remove spent shale, and note the coking tendencies (see below).

Coking Tendency	Condition of Shale
None (N)	Removes easily from retort; no coking tendency noted
Slight (S)	Requires a spatula for complete removal of shale from the retort
Moderate (M)	Partially fused, difficult to remove shale from the retort
Heavy (H)	Completely fused, very difficult to remove shale from the retort

19. Clean up retort, glass, tube and plug for the next assay.

CAUTION:

All calculations are performed on the Fischer Assay Sheet (F-1-3). Instructions are defined on the sheet.

NOTE 1: Since the time consuming specific gravity determination usually produces a repeatable value, a specific gravity of 0.915 may be assumed. Determination of oil yield, gallon then equivalent to 2.615 x oil yield, wt. The specific gravity determination (as described in F-0-10) should be done periodically.

Report on the Fischer Assay Report (F-1-3) the following:

Sample description: "raw" or "spent"

Date of sample: month/date/year

Time of sample: military time

Retort run number, sample number

NOTE: The above information should appear on the sample tag.

Oil, wt to nearest 0.01 wt

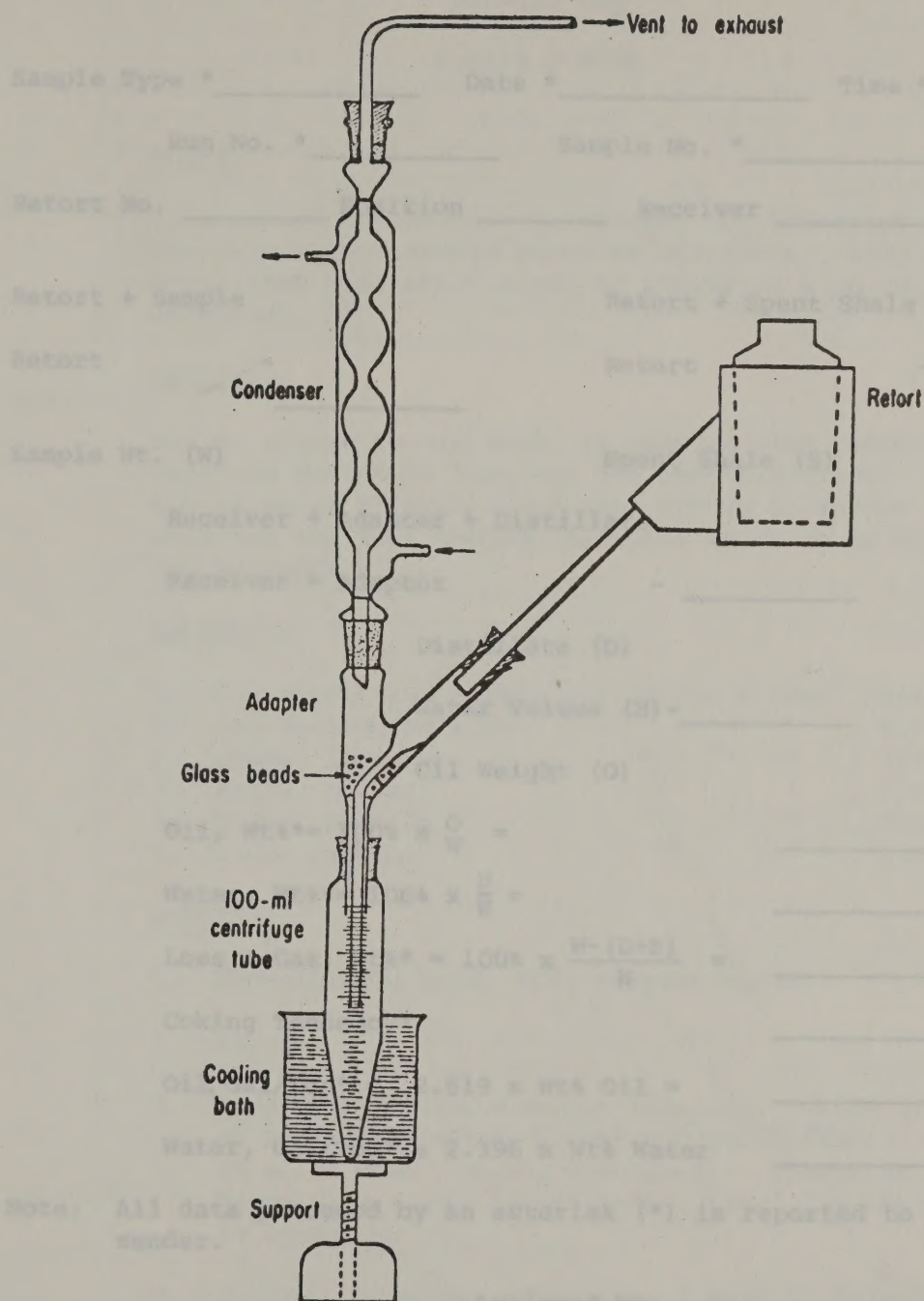
Water, wt to nearest 0.01 wt

Loss + Gas to nearest 0.01 wt

Coking tendency: "none", "slight", "moderate", or "heavy."

Oil, Gallon to nearest 0.1 gal

Water, Gallon to nearest 0.1 gal

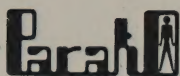


### Fischer Assay Distillation Apparatus

Figure 2-1







## PARAHO PROJECT

## FISCHER ASSAY SHEET

Sample Type \* \_\_\_\_\_ Date \* \_\_\_\_\_ Time \* \_\_\_\_\_

Run No. \* \_\_\_\_\_ Sample No. \* \_\_\_\_\_

Retort No. \_\_\_\_\_ Position \_\_\_\_\_ Receiver \_\_\_\_\_

Retort + Sample \_\_\_\_\_ Retort + Spent Shale \_\_\_\_\_

Retort - \_\_\_\_\_ Retort - \_\_\_\_\_

Sample Wt. (W) \_\_\_\_\_ Spent Shale (S) \_\_\_\_\_

Receiver + Adapter + Distillate \_\_\_\_\_

Receiver + Adapter - \_\_\_\_\_

Distillate (D) \_\_\_\_\_

Water Volume (H) - \_\_\_\_\_

Oil Weight (O) \_\_\_\_\_

$$\text{Oil, Wt\%} = 100\% \times \frac{O}{W} = \underline{\hspace{2cm}}$$
$$\text{Water, Wt\%} = 100\% \times \frac{H}{W} = \underline{\hspace{2cm}}$$
$$\text{Loss + Gas, Wt\%} = 100\% \times \frac{W - (D + S)}{W} = \underline{\hspace{2cm}}$$

Coking Tendency\* \_\_\_\_\_

Oil, Gal/Ton\* =  $2.619 \times \text{Wt\% Oil}$  = \_\_\_\_\_Water, Gal/Ton\* =  $2.396 \times \text{Wt\% Water}$  = \_\_\_\_\_

Note: All data preceded by an asterisk (\*) is reported to sender.

Analyzed by: \_\_\_\_\_

Date: \_\_\_\_\_

Reported by: \_\_\_\_\_



6-1-3

PARAMO PROJECT

FINCHER ASSAY SHEET

Sample Type \* \_\_\_\_\_ Date \* \_\_\_\_\_ Time \* \_\_\_\_\_  
Run No. \* \_\_\_\_\_ Sample No. \* \_\_\_\_\_  
Retort No. \_\_\_\_\_ Position \_\_\_\_\_ Receiver \_\_\_\_\_  
Retort + Sample \_\_\_\_\_ Retort + Spent Shale \_\_\_\_\_  
Retort \_\_\_\_\_ Retort \_\_\_\_\_

Sample Wt. (W) \_\_\_\_\_ Spent Shale (S) \_\_\_\_\_

Receiver + Adapter + Distillate \_\_\_\_\_  
Receiver + Adapter \_\_\_\_\_

Distillate (D) \_\_\_\_\_

Water Volume (H) \_\_\_\_\_

Oil Weight (O) \_\_\_\_\_

$$\text{Oil, Wt\%} = 100 \times \frac{O}{W}$$

$$\text{Water, Wt\%} = 100 \times \frac{H}{W}$$

$$\text{Loss + Gas, Wt\%} = 100 \times \frac{W - (D+S)}{W}$$

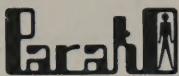
Coking Tendency\* \_\_\_\_\_

$$\text{Oil Gal/Ton} = 2.619 \times \text{Wt\% Oil}$$

$$\text{Water Gal/Ton} = 2.204 \times \text{Wt\% Water}$$

Note: All data preceded by an asterisk (\*) is reported to number.

Analyzed by: \_\_\_\_\_  
Data: \_\_\_\_\_  
Reported by: \_\_\_\_\_



## PROCEDURE FOR ASSEMBLING APPARATUS

### PARAHO OIL SHALE DEMONSTRATION

#### Mineral CO<sub>2</sub>

#### Method P-S-02

#### SCOPE:

This method determines the mineral CO<sub>2</sub> liberated from the carbonate minerals found in oil shale. Acid gases, other than H<sub>2</sub>S, which might be liberated with CO<sub>2</sub>, will interfere.

#### OUTLINE:

Shale, ground to -100 mesh, is reacted with hydrochloric acid and heated to liberate the carbon dioxide. The CO<sub>2</sub> is swept through a scrubber system to remove H<sub>2</sub>S and moisture and then through Ascarite where it is absorbed and weighed.

#### APPARATUS:

1. CO<sub>2</sub> Distilling Flask, Sci. Glass & Inst., 8540
2. Gas Washing Bottles, " " , 2121
3. Midget Impinger, " " , 16312
4. Bulbs, Midvale, " " , 2190
5. Bulbs, Nesbitt, " " , 2200
6. Tube, Drying, " " , 11052

#### REAGENTS:

1. Hydrochloric Acid, HCl, reagent grade.
2. Aerosol
3. Cadmium Chloride Absorber Solution. Weigh 20 gm. of CdCl<sub>2</sub> into about 500 ml H<sub>2</sub>O (distilled). Add 30 ml of conc. H<sub>2</sub>SO<sub>4</sub> (caution!). Dilute to 1.0 liter with water (distilled). Label "2% CdCl<sub>2</sub> in 1N H<sub>2</sub>SO<sub>4</sub>."
4. Calcium Chloride, Anhydrous, 8 mesh or Drierite.
5. Magnesium Perchlorate, 10-20 mesh.
6. Ascarite, 8-20 mesh.
7. Glass Wool.



# TAMAROC OIL SHALE DEMONSTRATION

Mineral  $\text{CO}_2$

Method P-2-02

## SCOPE:

This method determines the mineral  $\text{CO}_2$  liberated from the carbonate minerals found in oil shale. Acid gases, other than  $\text{H}_2\text{S}$ , which might be liberated with  $\text{CO}_2$ , will interfere.

## OUTLINE:

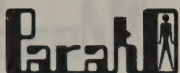
Shale, ground to -100 mesh, is reacted with hydrochloric acid and heated to liberate the carbon dioxide. The  $\text{CO}_2$  is swept through a scrubber system to remove  $\text{H}_2\text{S}$  and moisture and then through Ascarite where it is absorbed and weighed.

## APPARATUS:

1.	$\text{CO}_2$ Gas Measuring Flask, 500 ml. Glass & Inert.	8540
2.	Gas Washing Bottles.	2121
3.	Midcot Impinger.	16312
4.	Bulbs, Methyl.	2190
5.	Bulbs, Methyl.	2190
6.	Tube, Drying.	21022

## REAGENTS:

1. Hydrochloric Acid, HCl, reagent grade.
2. Acetone.
3. Calcium Chloride Absorber Solution. Weigh 20 gm of  $\text{CaCl}_2$  into about 500 ml  $\text{H}_2\text{O}$  (distilled). Add 10 ml of conc.  $\text{H}_2\text{SO}_4$  (caution). Dilute to 1.0 liter with water (distilled). Label "2%  $\text{CaCl}_2$  in  $\text{H}_2\text{SO}_4$ ".
4. Calcium Chloride, Anhydrous, 8 mesh or finer.
5. Magnesium Perchlorate, 10-20 mesh.
6. Ascarite, 8-20 mesh.
7. Glass Wool.



## PROCEDURE FOR ASSEMBLING APPARATUS

1. Fill gas washing bottles about one-half full of the cadmium chloride absorber solution.
2. Place a wad of glass wool in the bottom of the Midvale absorbers. Fill the first with calcium chloride and the second with magnesium perchlorate. Place another plug of glass wool on the top and stopper both bottles. Label each to identify the contents.
3. Prepare several Nesbitt bulbs by placing wads of glass wool in each. Fill about 2/3 with Ascarite and the remainder with magnesium perchlorate. Place another plug of glass wool on the top and stopper all bottles. Identify each absorber using a convenient numbering system.
4. Assemble the absorption train as shown in Figure 2-2, making sure there are no leaks at the joints.

## PROCEDURE

1. Purge the entire apparatus (as shown in Figure 2-2) 45 minutes; stop flow and disconnect the Nesbitt bulbs (see note 1).
2. Weigh about 1 gm (to nearest 0.1 mg) of sample (ground to -100 mesh) into a weighing vial.
3. Transfer the contents of the vial to the reaction flask; add about 2 ml of aerosol; wash into the flask with sufficient distilled water to cover inlet tip.
4. Weigh two Nesbitt bulbs (see Note 2) to the nearest 0.1 mg.
5. Attach bulbs to apparatus as shown in Figure 2-2 and connect vacuum.
6. Open all stop cocks to draw clean air through the system at 100cc/minute.
7. Add 20 ml of hydrochloric acid to the reservoir; turn stop cock (A) (see Figure 2-2) so that the acid drains slowly into the reaction flask.
8. Turn stop cock (A) to admit air to the system.
9. Heat solution in the reaction flask slowly until the solution boils, continue heating for about five minutes.
10. Remove heat and purge for 45 minutes.
11. Close all stop cocks and shut off vacuum.
12. Remove Nesbitt bulbs and allow to cool at room temperature for about 30 minutes.
13. Reweigh Nesbitt bulbs to nearest 0.1 mg (see Note 2).

## CALCULATIONS:

$$\text{Mineral CO}_2: \frac{T \text{ (gm)} - B \text{ (gm)}}{\text{Sample Wt (gm)}} \times 100\%$$

$$T = \text{Total Weight Gain} = [\text{Bulb 1 (final)} - \text{Bulb 1 (orig.)}] + [\text{Bulb 2 (final)} - \text{Bulb 2 (orig.)}]$$

Note: If [Bulb 2 (final) - Bulb 2 (orig.)] is greater than 5 mg the test must be rerun.

$$B = \text{Total Blank} = [\text{Bulb 1 (final)} - \text{Bulb 1 (orig.)}] + [\text{Bulb 2 (final)} - \text{Bulb 2 (orig.)}]$$



# PROCEDURE FOR ASSEMBLING APPARATUS

1. Fill gas washing bottles about one-half full of the cadmium chloride absorber solution.
2. Place a pad of glass wool in the bottom of the Midvale absorbers. Fill the first with calcium chloride and the second with magnesium perchlorate. Place another plug of glass wool on the top and stopper both bottles. Label each to identify the contents.
3. Prepare several Nesbitt bulbs by placing wads of glass wool in each. Fill about 2/3 with Anarsite and the remainder with magnesium perchlorate. Place another plug of glass wool on the top and stopper all bottles. Identify each absorber using a convenient numbering system.
4. Assemble the absorption train as shown in Figure 2-2, making sure there are no leaks at the joints.

## PROCEDURE

1. Purge the entire apparatus (as shown in Figure 2-2) 45 minutes; stop flow and disconnect the Nesbitt bulbs (see note 1).
2. Weigh about 1 gm (to nearest 0.1 mg) of sample (ground to -100 mesh) into a weighing vial.
3. Transfer the contents of the vial to the reaction flask; add about 2 ml of anarsite; wash into the flask with sufficient distilled water to cover inlet tip.
4. Weigh two Nesbitt bulbs (see Note 2) to the nearest 0.1 mg.
5. Attach bulbs to apparatus as shown in Figure 2-2 and connect vacuum.
6. Open all stop cocks to draw clean air through the system at 100cc/minute.
7. Add 50 ml of hydrochloric acid to the reservoir; turn stop cock (A) (see Figure 2-2) so that the acid drains slowly into the reaction flask.
8. Turn stop cock (A) to admit air to the system.
9. Heat solution in the reaction flask slowly until the solution boils, continue heating for about five minutes.
10. Remove heat and purge for 45 minutes.
11. Close all stop cocks and shut off vacuum.
12. Remove Nesbitt bulbs and allow to cool to room temperature for about 30 minutes.
13. Reweigh Nesbitt bulbs to nearest 0.1 mg (see Note 2).

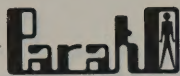
## CALCULATIONS:

$$\text{Mineral CO}_2 = \frac{T (\text{gm}) - B (\text{gm})}{\text{Sample Wt (gm)}} \times 100\%$$

$$T = \text{Total Weight Gain} = [\text{Bulb 1 (final)} - \text{Bulb 1 (orig.)}] + [\text{Bulb 2 (final)} - \text{Bulb 2 (orig.)}]$$

Notes: 1. [Bulb 2 (final) - Bulb 2 (orig.)] is greater than 2 mg the test must be rerun.

$$B = \text{Total Blank} = [\text{Bulb 1 (final)} - \text{Bulb 1 (orig.)}] + [\text{Bulb 2 (final)} - \text{Bulb 2 (orig.)}]$$



Report Mineral CO<sub>2</sub> (or mineral C) to nearest 0.01% on report sheet P-L-1

PRECISION:

Repeatability: Duplicate results should agree with 0.45 wt%.

Note 1:

Blanks should be run at least once (for each train) during a two week period. Blanks are run according to PROCEDURE (omit steps 2 & 3). If blanks are greater than 5 mg, the test should be rerun.

Note 2:

Since the prepared Nesbitt bulb weighs greater than 100 gm and has a volume of nearly 50 ml, great care must be taken to obtain true weights to the nearest 0.1 mg. The following procedure is recommended:

1. Always store the bulbs with the stop cocks closed to the atmosphere.
2. Vent the stop cocks momentarily before weighing to eliminate any pressure or vacuum in the bulb.
3. Be sure the bulbs are at room temperature before weighing.
4. Carefully wipe the surface with a clean chamois to remove absorbed moisture or traces of grease from fingerprints. Handle with care.
5. Remove any static just before weighing by brushing lightly with a special static-eliminator brush.



Report Mineral Co. (as nearest 0.01% on report sheet P-1-1)

PROCEDURE

Repeatability. Duplicate results should agree with 0.45 wt%.

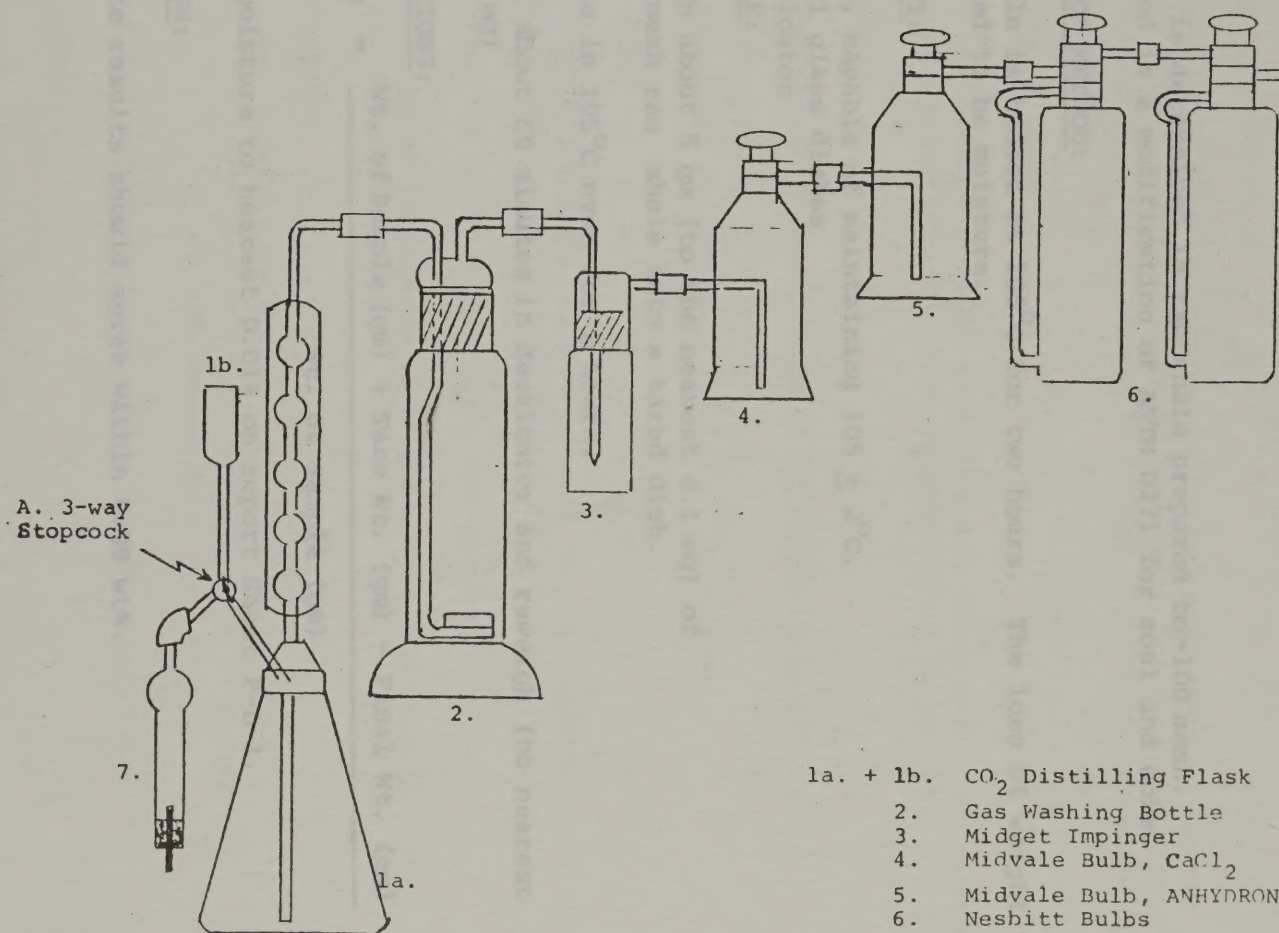
Note 1:

Blanks should be run at least once (for each trial) during a two week period. Blanks are run according to PROCEDURE (omit steps 3 & 4). If blanks are greater than 5 mg, the test should be rerun.

Note 2:

Since the prepared Nessler bulb weighs greater than 100 gm and has a volume of nearly 30 ml, great care must be taken to obtain true weights to the nearest 0.1 mg. The following procedure is recommended.

1. Always store the bulbs with the stop cocks closed to the atmosphere.
2. Vent the stop cocks momentarily before weighing to eliminate any pressure or vacuum in the bulb.
3. Be sure the bulbs are at room temperature before weighing.
4. Carefully wipe the surface with a clean cloth to remove absorbed moisture or traces of grease from fingerprints. Handle with care.
5. Remove any static just before weighing by brushing lightly with a special static-eliminator brush.



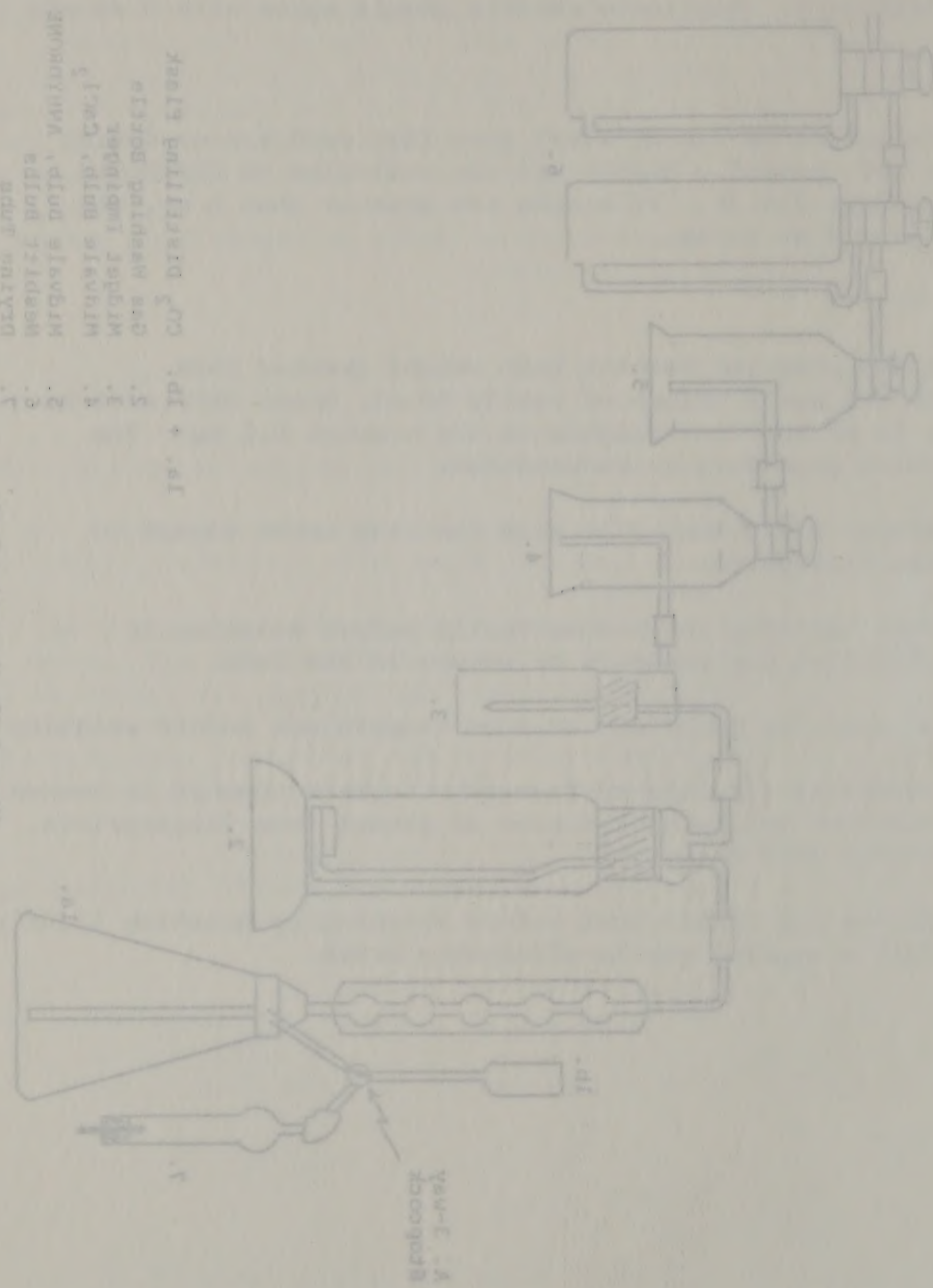
Mineral CO<sub>2</sub> Absorption Train

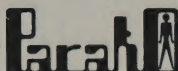
Figure 2-2



Рис. 3-3

Схема установки для





## PARAHO OIL SHALE DEMONSTRATION

### Moisture in Laboratory Shale Sample

#### Method P-S-03

#### SCOPE:

Moisture is determined in raw shale prepared to -100 mesh. The method is a modification of ASTM D271 for coal and coke.

#### OUTLINE OF METHOD:

The sample is heated at 105°C for two hours. The loss of weight is assumed to be moisture.

#### EQUIPMENT:

1. Oven, capable of maintaining 105 ± 2°C.
2. 50 ml glass dishes
3. Dessicator

#### PROCEDURE:

1. Weigh about 5 gm (to the nearest 0.1 mg) of -100 mesh raw shale into a tared dish.
2. Place in 105°C oven for 2 hours.
3. Cool about 60 minutes in dessicator and reweigh (to nearest 0.1 mg)

#### CALCULATIONS:

$$\text{Moisture} = \frac{\text{Wt. of Sample (gm)} + \text{Tare Wt. (gm)} - \text{Final Wt. (gm)}}{\text{Wt. of Sample (gm)}} \times 100\%$$

Report moisture to nearest 0.01% on report Sheet P-L-1.

#### PRECISION:

Duplicate results should agree within 0.09 wt%.



PARANO OIL SHALE DEMONSTRATION

Moisture in Laboratory Shale Sample

Method P-2-03

SCOPE:

Moisture is determined in raw shale prepared to -100 mesh. The method is a modification of ASTM D371 for coal and coke.

OUTLINE OF METHOD:

The sample is heated at 105°C for two hours. The loss of weight is assumed to be moisture.

EQUIPMENT:

1. Oven, capable of maintaining 105 ± 2°C.
2. 50 ml glass dish
3. Desiccator

PROCEDURE:

1. Weigh about 5 gm (to the nearest 0.1 mg) of -100 mesh raw shale into a tared dish.
2. Place in 105°C oven for 2 hours.
3. Cool about 30 minutes in desiccator and reweigh (to nearest 0.1 mg)

CALCULATIONS:

$$\text{Moisture} = \frac{\text{Wt. of Sample (gm)} + \text{Tare Wt. (gm)} - \text{Final Wt. (gm)}}{\text{Wt. of Sample (gm)}} \times 100\%$$

Report moisture to nearest 0.01% on report Sheet P-2-1.

PRECISION:

Duplicate results should agree within 0.02 wt%.



## PARAHO OIL SHALE DEMONSTRATION

### Ash in Shale

### Method P-S-04

#### SCOPE:

The ash content is determined in shales prepared to -100mesh. The method is a modification of ASTM D271 for coal and coke, however the temperature is increased to 1800°F (982°C) to decompose the mineral carbonates.

#### OUTLINE OF METHOD:

Shale samples are ignited at 1800°F for two hours. The portion remaining after this ignition is considered to be ash.

#### EQUIPMENT:

1. Heavy-duty furnace, capable of maintaining 1800  $\pm$  50°F
2. Dessicator
3. Porcelain crucibles.

#### PROCEDURE:

1. Weigh about 2 gm (to nearest 0.1 mg) of -100mesh shale into a tared crucible.
2. Place in 1800°F furnace for two hours.
3. Cool about 60 minutes in a dessicator and reweigh (to nearest 0.1 mg)

#### CALCULATIONS:

$$\text{Ash, Wt\%} = \frac{\text{Final Wt (gm)} - \text{Tare Wt (gm)}}{\text{Wt. of Sample (gm)}} \times 100\%$$

Report ash to nearest 0.01 wt% on report sheet P-L-1.

#### PRECISION:

Duplicate results should agree within 1.11 wt%.

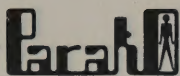


1200

WESTON BOND

100 PERCENT

25X COTTON FIBER



## PARAHO OIL SHALE DEMONSTRATION

### Elemental Analysis

(Total Carbon, Hydrogen and Nitrogen)

Method P-S-05

#### SCOPE:

This method determines total carbon, hydrogen and nitrogen in raw or retorted shale. Also, the ash content (wt% ash) can be determined. Ash values are comparable to those obtained by Method P-S-04. Comparison with other laboratories and repeatability of the elemental analyses are generally less than 0.2 wt%.

#### OUTLINE:

A suitable sample (5-11 mg) is carefully weighed and placed into the combustion zone. There, combustion in a pure oxygen atmosphere at 1000°C occurs. Excess oxygen is removed and oxides of nitrogen are reduced to molecular nitrogen in the reduction tube. The remaining mixture (carbon dioxide, water vapor, and nitrogen) are mixed with a helium carrier gas. The mixture is determined sequentially using a series of solenoid valves, absorption tubes, and thermal conductivity detectors.

#### EQUIPMENT:

The Perkin-Elmer Model 240 Elemental Analyzer is ideally suited for the determination of total C, H, and N in oil shale materials.

1. Model 240 Elemental Analyzer, 240-0001.
2. Single Channel Recorder, P-E 056-0017.
3. Autobalance, Model AM-2, 322-0007.
4. Sample Handling Accessory Kit, 240-0081.
5. Platinum Boat Kit, 240-0090.
6. Helium, High Purity (99.995%), Linde.
7. Oxygen, Ultra High Purity (99.99%), Linde.
8. High Purity Regulators, 240-0084, 240-0085.

#### PROCEDURE:

##### A. Initial Start Up

1. Refer to PE 240 Manual, pg. 1-8, Section 1-I
2. Fill time should be between 120-180 sec.

##### B. Daily Start Up

1. Refer to PE 240 Manual, pg. 3-7, Section 3-E1, and note the following changes:



PARADOX SHALE DEMONSTRATION

Elemental Analysis

(Total Carbon, Hydrogen and Nitrogen)

Revised 9-8-65

SCOPE:

This method determines total carbon, hydrogen and nitrogen in raw or retorted shale. Also, the ash content (wt% ash) can be determined. Ash values are comparable to those obtained by Method P-8-64. Comparison with other laboratories and repeatability of the elemental analysis are generally less than 0.5 wt%.

OUTLINE:

A suitable sample (2-11 wt) is carefully weighed and placed into the combustion zone. There, combustion in a pure oxygen atmosphere at 1800°C occurs. Excess oxygen is removed and oxides of nitrogen are reduced to molecular nitrogen in the reduction tube. The remaining mixture (carbon dioxide, water vapor, and nitrogen) are mixed with a helium carrier gas. The mixture is determined sequentially using a series of solenoid valves, absorption tubes, and thermal conductivity detectors.

EQUIPMENT:

The Beckman-Elmer Model 240 Elemental Analyzer is ideally suited for the determination of total C, H, and N in oil shale materials.

1. Model 240 Elemental Analyzer, 240-0001
2. Single Channel Recorder, R-2 328-0017
3. Autoanalyzer, Model RM-2, 123-0007
4. Sample Handling Accessory Kit, 240-0001
5. Platinum Boat Kit, 240-0003
6. Helium, high purity (99.999%), 1 liter
7. Oxygen, ultra high purity (99.999%), 1 liter
8. High Purity Regulators, 240-0004, 240-0005

PROCEDURE:

A. Initial Start Up

1. Refer to PE 240 Manual, pp. 1-8, Section 1-1
2. Fill time should be between 150-160 sec.

B. Daily Start Up

1. Refer to PE 240 Manual, pp. 3-7, Section 3-11, and note the following changes:

- a. Programmer index wheel is at 9
- b. Furnace temperature setting is 1000°C
- c. During the run, the program lamp should go off about 2 min. 20 sec. after the combustion button is pushed and should remain off for 120-180 sec.
- d. Run two unweighed samples before a blank is run.

2. Typical values for blanks are given in Table 3-2; for  $K_x$  in Table 3-4; see PE Manual PP 3-6, 3-7.

- a. If blank or  $K_x$  values are outside those ranges, refer to PE 240 Manual, pg. 4-2, Section 4C.

#### C. Daily Shutdown

1. Refer to PE 240 Manual, pg. 3-9, Section 3-E2, and note the following changes:
  - a. Set programmer index wheel at 9
  - b. Lower furnace temperature to 900°C

#### D. Power Shutdown

1. Refer to PE 240 Manual, pg 3-9, Section 3-E2

#### E. Blank Run

1. Refer to PE 240 Manual, pg. 3-5, Section 3-C
2. Compare blank value with values given in the table under "Daily Start Up."

#### F. Calibration

1. Refer to PE 240 Manual, pg 3-7, Section 3D-2
2. Also note, Calibration Check, Section 3D-3
3. Compare sensitivity values ( $K_x$ ) with values given in the table under "Daily Start Up."
4. Do all calculations on the Calibration Data Sheet, P-L-8.

#### G. Sample Analysis

1. Refer to PE 240 Manual, pg 3-1, Sections 3A and 3B, and note the following changes:



- a. Proprietary index wheel is at 2
  - b. Furnace temperature setting is 1000°C
  - c. During the run, the program lamp should go off about 2 min. before the combustion button is pushed and should remain off for 10-150 sec.
  - d. Run two unweighed samples before a blank is run.
2. Typical values for blanks are given in Table 1-1. For K<sub>2</sub> in Table 1-4; see PE Manual, pp. 3-4, 3-7.
3. If blank or K<sub>2</sub> values are outside those ranges, refer to PE 340 Manual, pp. 4-2, Section 4C.
- C. Daily Shutdown
1. Refer to PE 340 Manual, pp. 3-7, Section 3-2, and note the following changes:
    - a. Set proprietary index wheel at 2
    - b. Lower furnace temperature to 200°F
- D. Power Shutdown
1. Refer to PE 340 Manual, pp. 3-2, Section 3-2.
- E. Blank Run
1. Refer to PE 340 Manual, pp. 3-2, Section 3-2.
  2. Compare blank values with values given in the table under "Daily Start Up."
- F. Calibration
1. Refer to PE 340 Manual, pp. 3-7, Section 3D-1.
  2. Also note, Calibration Check, Section 3D-1.
  3. Compare sensitivity values (K<sub>2</sub>) with values given in the table under "Daily Start Up."
  4. Do all calculations on the Calibration Data Sheet, P-1-B.
- G. Sample Analysis
1. Refer to PE 340 Manual, pp. 3-1, Section 3A and 3B, and note the following changes:

# CALIBRATION DATA SHEET

A. Standard Name:

B. Date:

- a. Use 5-11 mg shale sample.
- b. No oxygen donors or other oxidation aids are used.

C. Standard Weight:

D. Sample:

E. C:

F. D

2. Do all calculations on the Data Sheet for Samples, P-L-9.

H. Theoretical Weights:

mg B:

mg C:

mg H

3. Report results on Report Sheet, PL-1.

I. Total Signal:

## H. Servicing and Maintenance

Total Signal (in mv) = Read + C Suppression - Blank Value - Zero

Where:

Read or

Blank

1. Refer to PE 240 Manual, pg. 4-1, Sections 4A, 4B and 4C. The operator of the analyzer should read and thoroughly understand these sections before any problems develop.

2. Replacing traps and scrubbers. Refer to PE 240 Manual, pg. 4-11, Sections 4E-4a and 4E-4b and PE looseleaf handout.

Note: Before turning power switch to "detect," wait 5 min. to be sure safety circuit lamp does not light.

3. Replacing combustion and reduction tubes. Refer to PE 240 Manual, pg 4-11, Sections 4E-5 and 4E-6 and PE looseleaf handout.

4. Replacing helium cylinder. Refer to PE 240 Manual, pg. 4-13, Section 4E-7.

5. Replacing oxygen cylinder. Refer to PE looseleaf handouts.

G. Sensitivity:

Total signal (mv)

X = Theoretical Weight (mg)

mv

mg

mv

mg

mv

mg

\*Values of C Suppression of C ADJUSTMENT Switch Settings.

(Use in computation of C signal only.)

Switch Setting	0	1	2	3	4	5
C Suppression (mv)	0	10,000	20,000	30,000	40,000	50,000



- a. Use 5-11 as sample.
- b. No oxygen demand or other oxidation aids are used.

- 1. Do all calculations on the Data Sheet for Samples, P-1-3.
- 2. Report results on Report Sheet, P-1-1.

#### B. Servicing and Maintenance

- 1. Refer to PE 340 Manual, pp. 4-1, Section 4B, 4C and 4D. The operator of the analyzer should read and thoroughly understand these sections before any problems develop.

- 2. Replacing traps and scrubbers. Refer to PE 340 Manual, pp. 4-11, Sections 4B-4a and 4B-4b and PE 1000000 handbook.

Note: Before turning power switch to "On", wait 2 min. to be sure safety circuit lamp does not light.

- 3. Replacing condenser and reduction tubes. Refer to PE 340 Manual, pp. 4-11, Sections 4B-2 and 4B-3 and PE 1000000 handbook.

- 4. Replacing helium cylinder. Refer to PE 340 Manual, pp. 4-11, Section 4B-7.

- 5. Replacing oxygen cylinder. Refer to PE 1000000 handbook.



## DATA SHEET FOR SAMPLES

## CALIBRATION DATA SHEET

A. Sample No.: \_\_\_\_\_ B. Sample Name: \_\_\_\_\_

C. Standard Weight: \_\_\_\_\_ ug

D. Theoretical Percentages : \_\_\_\_\_ % N; \_\_\_\_\_ % C; \_\_\_\_\_ % H

E. Theoretical Weights: \_\_\_\_\_ ug N; \_\_\_\_\_ ug C; \_\_\_\_\_ ug H

F. Total Signals:

Total Signal (in uV) = Read + C Suppression\* - Blank Value - Zero

Where:

Read or Zero (in uV) = (Recorder Reading X10) (Attenuation)

Blank Value (in uV) = Blank Read - Blank Zero

	<u>N Signal</u>	<u>C Signal</u>	<u>H Signal</u>
Reads (uV)	_____ X _____ = _____	_____ X10 = _____	_____ X _____ = _____
+ C Suppression* (uV)	****	Setting _____ = _____	***
- Blank Values (uV)	_____ = _____	_____ = _____	_____ = _____
- Zeros (uV)	_____ X _____ = _____	_____ X10 = _____	_____ X _____ = _____
Total Signals (uV)	_____ = _____	_____ = _____	_____ = _____

G. Sensitivities:

$$K = \frac{\text{Total signal (uV)}}{\text{Theoretical Weight (ug)}}$$

$$K_N \frac{\text{uV}}{\text{ug}}; K_C \frac{\text{uV}}{\text{ug}}; K_H \frac{\text{uV}}{\text{ug}}$$

\*Values of C Suppression of C ATTENUATION Switch Settings.  
(Use in Computation of C Signal Only.)

Switch Setting	0	1	2	3	4	5
C Suppression (uV)	0	10,000	20,000	30,000	40,000	50,000



# CALIBRATION DATA SHEET

A. Standard Name: \_\_\_\_\_ B. Date: \_\_\_\_\_

C. Standard Weight: \_\_\_\_\_

D. Theoretical Percentages: \_\_\_\_\_

E. Theoretical Weights: \_\_\_\_\_

F. Total Signals: \_\_\_\_\_

Total Signal (in uv) = Read + C Suppression\* - Blank Value - Zero

Notes:

\* Read or Zero (in uv) = Recorder Reading X101 (attenuation)

Blank Value (in uv) = Blank Read - Blank Zero

Read (uv)	+ C Suppression* (uv)	- Blank Value (uv)	- Zero (uv)	Total Signal (uv)
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____

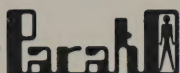
G. Sensitivity:

Total signal (uv)  
K = Theoretical Weight (ug)

\_\_\_\_\_ uv \_\_\_\_\_ uv \_\_\_\_\_ uv  
\_\_\_\_\_ ug \_\_\_\_\_ ug \_\_\_\_\_ ug

\*Values of C Suppression of C ATTENUATION Switch Settings.  
(Use in Calculation of C Signal Only.)

C Suppression (uv)	Switch Setting
10,000	1
10,000	2
10,000	3
10,000	4
10,000	5



## DATA SHEET FOR SAMPLES

- A. Sample No.: \_\_\_\_\_ B. Sample Name: \_\_\_\_\_
- C. Date: \_\_\_\_\_ D. Sample Weight: \_\_\_\_\_ ug
- E. Theoretical Percentages: \_\_\_\_\_ %N; \_\_\_\_\_ %C; \_\_\_\_\_ %H
- F. Theoretical Weights: \_\_\_\_\_ ug N; \_\_\_\_\_ ug C; \_\_\_\_\_ ug H
- G. Sensitivities:  $K_N = \frac{\text{uV}}{\text{ug}}$ ;  $K_C = \frac{\text{uV}}{\text{ug}}$ ;  $K_H = \frac{\text{uV}}{\text{ug}}$
- H. Total Signals:

Total Signal (in uV) = Read + C Suppression\* - Blank Value - Zero

where:

Read or Zero (in uV) = (Recorder Reading X10) (Attenuation)

Blank Value (in uV) = Blank Read - Blank Zero

	N Signal	C Signal	H Signal
Reads (uV)	<u>    X    </u> = _____	<u>    X10    </u> = _____	<u>    X    </u> = _____
+ C Suppression* (uV)	<u>    ***    </u>	Setting <u>    </u> = _____	<u>    ***    </u>
- Blank Values (uV)	<u>    </u> = _____	<u>    </u> = _____	<u>    </u> = _____
- Zeros (uV)	<u>    X    </u> = _____	<u>    X10    </u> = _____	<u>    X    </u> = _____
Total Signals (uV)	<u>    </u> = _____	<u>    </u> = _____	<u>    </u> = _____

## I. Calculated Weights and Percentages:

Weight (ug) of N, C, or H in a sample =  $\frac{\text{Total signal (uV)}}{\text{Sensitivity K ug}}$

Weights \_\_\_\_\_ ug N; \_\_\_\_\_ ug C; \_\_\_\_\_ ug H

Percentage of N, C, or H in a sample =  $\frac{\text{Weight (ug)} \times 100}{\text{Sample Weight}}$

Percentages \_\_\_\_\_ % N; \_\_\_\_\_ % C; \_\_\_\_\_ % H

\*Values of C Suppression for C ATTENUATION Switch Settings.  
(Use in Computation of C Signal Only.)

Switch Setting	0	1	2	3	4	5
C Suppression (uV)	0	10,000	20,000	30,000	40,000	50,000



DATA SHEET FOR SAMPLES

A. Sample No.: \_\_\_\_\_  
 B. Sample Name: \_\_\_\_\_  
 C. Date: \_\_\_\_\_  
 D. Sample Weight: \_\_\_\_\_  
 E. Theoretical Percentages: \_\_\_\_\_  
 F. Theoretical Weight: \_\_\_\_\_  
 G. Sensitivity:  $K = \frac{W}{W_0}$  \_\_\_\_\_  
 H. Total Signal: \_\_\_\_\_

Total Signal (in uv) = Read + C Suppression\* - Blank Value - Zero

where:

Read or Zero (in uv) = (Recorder Reading X10) (Assessment)

Blank Value (in uv) = Blank Read - Blank Zero

Read (uv)	+ C Suppression* (uv)	- Blank Value (uv)	- Zero (uv)	Total Signal (uv)
X	***	=	X	=
X10	Setting	=	X10	=
X	***	=	X	=
X10	Setting	=	X10	=
X	***	=	X	=
X10	Setting	=	X10	=

I. Calculated Weights and Percentages:

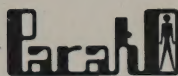
Weight (uv) of N, C, or H in a sample =  $\frac{\text{Total signal (uv)}}{\text{Sensitivity K uv}}$

Percentage of N, C, or H in a sample =  $\frac{\text{Weight (uv) x 100}}{\text{Sample Weight}}$

Percentages: N: \_\_\_\_\_ C: \_\_\_\_\_ H: \_\_\_\_\_

Values of C Suppression for C determination (each setting)  
 (Use in Computation of C Signal Only.)

Switch Setting	0	1	2	3	4	5
C Suppression (uv)	0	10,000	20,000	30,000	40,000	50,000



PRECISION:

Benzene-Soluble Material

No data available.

Method P-S-06

SCOPE:

This method is used to determine the benzene-soluble material in raw and retorted shale.

OUTLINE:

Using a Soxhlet apparatus and thimble, a weighed sample of shale is subjected to repeated soaking with fresh, hot benzene vapor.

APPARATUS:

Soxhlet extraction apparatus with appropriate thimbles.

REAGENTS:

Benzene, reagent grade.

Glass wool.

PROCEDURE:

1. Weigh about 10 gms to the nearest 0.1 mg into a tared thimble with glass wool.
2. Pack the glass wool on top of the sample.
3. Assemble the apparatus placing 100 ml of benzene in the flask.
4. Heat until the benzene is refluxing. Continue for 30 minutes. (If the Benzene becomes discolored, continue for an additional 30 minutes).
5. Allow system to cool, dry the thimble and contents for 1 hour at 105°C or until benzene odor is gone.
6. Allow the thimble and contents to cool in a dessicator for 1 hour; then reweigh to nearest 0.1 mg.

CALCULATIONS:

$$\text{Benzene-solubles, wt\%} = 100\% \times \frac{\text{Initial Wt (gm)} - \text{Final Wt (gm)}}{\text{Sample Wt (gms)}}$$

Initial Wt = Original Sample - Thimble

Final Wt = Dried, Refluxed Sample - Thimble



# PARAFFIN OIL SHALE WORKSTATION

## Benzene-Soluble Material

Method V-2-06

### SCOPE:

This method is used to determine the benzene-soluble material in raw and retorted shale.

### OUTLINE:

Using a Soxhlet apparatus and thimble, a weighed sample of shale is subjected to repeated soaking with fresh, hot benzene vapor.

### APPARATUS:

Soxhlet extraction apparatus with appropriate thimbles.

### REAGENTS:

Benzene, reagent grade.  
Glass wool.

### PROCEDURE:

1. Weigh about 10 gms to the nearest 0.1 mg into a tared thimble with glass wool.
2. Pack the glass wool on top of the sample.
3. Assemble the apparatus placing 100 ml of benzene in the flask.
4. Heat until the benzene is refluxing. Continue for 30 minutes. (If the benzene becomes discolored, continue for an additional 30 minutes).
5. Allow system to cool, dry the thimble and contents for 1 hour at 105°C or until benzene odor is gone.
6. Allow the thimble and contents to cool in a desiccator for 1 hour; then reweigh to nearest 0.1 mg.

### CALCULATIONS:

Benzene-solubles, wt% =  $100 \times \frac{\text{Initial Wt (gm)} - \text{Final Wt (gm)}}{\text{Sample Wt (gm)}}$

Initial Wt = Original Sample - Thimble  
Final Wt = Dried, Retained Sample - Thimble

Report benzene solubles to nearest 0.01 wt% on report sheet P-L-1.

PRECISION:

No data available.

LABORATORY PROCEDURES

Density - Air Pycnometer

Method Number P-S-07

SCOPE:

This method determines the density of shale samples using the Beckman Air Comparison Pycnometer. Samples must be less than 0.5 inch size and free from excessive water or oil.

PROCEDURE:

A weighed, clean sample of shale is placed in the sample cup of the Air Pycnometer. After the sample chamber is sealed, the chamber and a reference chamber are pressurized to a fixed value by the use of two pistons. The difference in the piston movement between the reference and sample is calibrated in sample volume (ml). The method is simple and nondestructive.

EQUIPMENT:

Beckman Air Comparison Pycnometer, Model 330.

PROCEDURE:

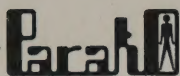
1. Determination of zero:
  - a. Close purge valve; open coupling valve.
  - b. Rotate both handwheels to counterclockwise extremes.
  - c. Turn measuring handwheel clockwise to starting number (107.50).
  - d. Place sample cup in cylinder and lock firmly.
  - e. After 15 seconds, close the coupling valve.
  - f. Turn both wheels clockwise until reference comes to the stop; keep the pointer on scale.
  - g. Adjust the sample wheel until the pointer is null (right marker).
  - h. Open the coupling valve, read zero from the counter (cc.), and record.
  - i. Turn both handwheels to counterclockwise extremes.
  - j. Remove sample cup and clean.



Report presents solutions to nearest 0.01 wt% on report sheet P-1-I.

PRECISION:

No data available.



## PARAHO OIL SHALE DEMONSTRATION

### LABORATORY PROCEDURE

#### Density - Air Pycnometer

#### Method Number P-S-07

#### SCOPE:

This method determines the density of shale samples using the Beckman Air Comparison Pycnometer. Samples must be less than 0.5 inch size and free from excessive water or oil.

#### PROCEDURE:

A weighed, clean sample of shale is placed in the sample cup of the Air Pycnometer. After the sample chamber is sealed, the chamber and a reference chamber are pressurized to a fixed value by the use of two pistons. The difference in the piston movement between the reference and sample is calibrated in sample volume (ml). The method is simple and nondestructive.

#### EQUIPMENT:

Beckman Air Comparison Pycnometer, Model 930.

#### PROCEDURE:

1. Determination of zero:
  - a. Close purge valve; open coupling valve.
  - b. Rotate both handwheels to counterclockwise extremes.
  - c. Turn measuring handwheel clockwise to starting number (107.60).
  - d. Place sample cup in cylinder and lock firmly.
  - e. After 15 seconds, close the coupling valve.
  - f. Turn both wheels clockwise until reference comes to the stop; keep the pointer on scale.
  - g. Adjust the sample wheel until the pointer is nulled (right marker).
  - h. Open the coupling valve, read zero from the counter (cc.), and record.
  - i. Turn both handwheels to counterclockwise extremes.
  - j. Remove sample cup and clean.



PARANO OIL SHALE DEMONSTRATION

LABORATORY PROCEDURE

Density - Air Pycnometer

Method Number P-2-07

SCOPE:

This method determines the density of shale samples using the Beckman Air Comparison Pycnometer. Samples must be less than 0.5 inch size and free from excessive water or oil.

PROCEDURE:

A weighed, clean sample of shale is placed in the sample cup of the Air Pycnometer. After the sample chamber is sealed, the chamber and a reference chamber are pressurized to a fixed value by the use of two pistons. The difference in the piston movement between the reference and sample is calibrated in sample volume (ml). The method is simple and nondestructive.

EQUIPMENT:

Beckman Air Comparison Pycnometer, Model 930.

PROCEDURE:

1. Determination of zero:

- a. Close purge valve; open coupling valve.
- b. Rotate both handwheels to counter-clockwise extremes.
- c. Turn measuring handwheel clockwise to starting number (107.60).
- d. Place sample cup in cylinder and lock firmly.
- e. After 15 seconds, close the coupling valve.
- f. Turn both wheels clockwise until reference comes to the stop; keep the pointer on scale.
- g. Adjust the sample wheel until the pointer is nullified (right marker).
- h. Open the coupling valve, read zero from the counter (cc.), and record.
- i. Turn both handwheels to counter-clockwise extremes.
- j. Remove sample cup and clean.

# PARAHO OIL SHALE DEMONSTRATION

## 2. Standard calibration:

### Particle Size Distribution, RoTap

- Reset measuring handwheel clockwise to starting number (107.60).
- Place stainless steel ball in the sample cup.
- Proceed as in "Determination of zero", steps d-j.
- Readings from step h should be: 1" ball, 8.58 cc; 1 3/16" ball, 14.37 cc.

## 3. Determination sample:

- Proceed as in "Standard calibration" using a sample (nearest 0.01 gm) instead of stainless steel ball in step b.
- After 5-10 determinations, zero should be rerun.

## CALCULATIONS:

$$\text{Density} = \frac{\text{Sample Wt (gm)}}{\text{Volume (cc)}}$$

Report density to nearest 0.001 gm/cc on report sheet P-L-1.

## PRECISION:

Duplicate results should agree within 0.036 gm/cc. Mean error is 0.46% (relative).

	Weight (gm)	Sieve Size	Opening (in.)
	0.850	10	0.093
	0.742	14	0.075
	0.624	20	0.046
	0.541	28	0.0325
	0.371	35	0.0232
2 1/2	0.312	48	0.0164
3	0.261	60	0.0118
4	0.195	80	0.0097
5	0.136	100	0.0059
6	0.131	150	0.0041
		200	0.0029

## PROCEDURE:

- Weigh sufficient sample (NOTE 1) to nearest 0.1 gm.
- Arrange proper sequence of sieves tared to the nearest 0.1 gm. (NOTE 2) with the largest opening on the top.
- Place the cover on the top, place stack on RoTap Sieve Shaker, and shake for five minutes.
- Obtain the weight of each sieve and pan.



2. Standard calibration:

- a. Reset measuring hardware clockwise to starting number (107.60).
- b. Place stainless steel ball in the sample cup.
- c. Proceed as in "Determination of zero", steps 6-7.
- d. Readings from step 6 should be: 1" ball, 9.28 cc; 1 3/16" ball, 14.37 cc.

3. Determination sample:

- a. Proceed as in "Standard calibration" using a sample (nearest 0.01 gm) instead of stainless steel ball in step b.
- b. After 5-10 determinations, zero should be return.

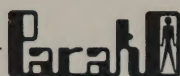
CALCULATION:

$$\text{Density} = \frac{\text{Sample Wt (gm)}}{\text{Volume (cc)}}$$

Report density to nearest 0.001 gm/cc on report sheet P-I-1.

PRECISION:

Duplicate results should agree within 0.036 gm/cc. Mean error is 0.46% (relative).



## PARAHO OIL SHALE DEMONSTRATION

### Particle Size Distribution, RoTap

#### Method P-S-08

#### SCOPE:

This method measures the particle size distribution of samples of raw or retorted shale submitted to the analytical laboratory or ground in the laboratory for specific analyses. Larger sized shale, such as the raw shale feed to the retorts or retorted shale direct from the retorts, is measured using the Ty-Lab Tester.

#### OUTLINE:

A weighed sample is placed on top of a stack of standard screens of increasing fineness. The entire stack is then shaken mechanically for a fixed time. The amount of sample on each screen and bottom pan is weighed and the size distribution is calculated.

#### APPARATUS:

1. RoTap Sieve Shaker
2. Standard Sieves, Cover and Bottom Pan

<u>Mesh Size</u>	<u>Opening (in.)</u>	<u>Mesh Size</u>	<u>Opening (in.)</u>
	1.25	7	0.110
	1.05	8	0.093
	0.883	10	0.078
	0.742	14	0.046
	0.624	20	0.0328
	0.441	28	0.0232
	0.371	35	0.0164
2 1/2	0.312	48	0.0116
3	0.263	60	0.0097
4	0.185	100	0.0058
5	0.156	150	0.0041
6	0.131	200	0.0029

#### PROCEDURE:

1. Weigh sufficient sample (NOTE 1) to nearest 0.1 gm.
2. Arrange proper sequence of sieves tared to the nearest 0.1 gm. (NOTE 2) with the largest opening on the top.
3. Place the cover on the top, place stack on RoTap Sieve Shaker, and shake for five minutes.
4. Obtain the weight of each sieve and pan.



# PARAFFIN OIL SHALE DEMONSTRATION

## Particle Size Distribution, Rotary

Method 2-2-08

### SCOPE:

This method measures the particle size distribution of samples of raw or retorted shale submitted to the analytical laboratory or ground in the laboratory for specific analyses. Larger sized shale, such as the raw shale feed to the retorts or retorted shale direct from the retorts, is measured using the Tyler Tester.

### OUTLINE:

A weighed sample is placed on top of a stack of standard screens of increasing fineness. The entire stack is then shaken mechanically for a fixed time. The amount of sample on each screen and bottom pan is weighed and the size distribution is calculated.

### APPARATUS:

1. Rotary Shale Shaker
2. Standard Sieves, Cover and Bottom Pan

Mesh Size	Opening (in.)	Mesh Size	Opening (in.)
1/2	0.150	7	0.118
3	0.085	8	0.093
4	0.075	10	0.075
5	0.063	14	0.048
6	0.053	20	0.038
		28	0.032
		35	0.025
		45	0.018
		60	0.0097
		100	0.0058
		150	0.0041
		200	0.0030

### PROCEDURE:

1. Weigh sufficient sample (NOTE 1) to nearest 0.1 gm.
2. Arrange proper sequence of sieves (NOTE 2) to the nearest 0.1 gm. (NOTE 3) with the coarsest opening on the top.
3. Place the cover on the top, place stack on Rotary Shale Shaker, and shake for five minutes.
4. Obtain the weight of each sieve and pan.

# CALCULATIONS:

1. Determine the weight of shale on each sieve and pan.
2. Add the weights of shale together to determine the total final weight (F).
3. Determine the percent of shale on each sieve and pan by  
% size (NOTE 3) =  $100\% \times \text{net wt (gm)} / F(\text{gm})$ .
4. Determine the overall recovery by:  
% recovery =  $100\% \times F(\text{gm}) / \text{sample wt (gm)}$

NOTE 1: Proper sample size depends upon the mesh size of the sample being measured. For the types of samples normally analyzed in the laboratory the proper sample sizes are: received shale (-1/4"), 500 gm; Fischer Assay (-20 mesh), 250 gm; "fine grind" (-65 mesh), 100 gm.

NOTE 2: In order to obtain normal distribution, the sieves should be arranged in numerical sequence (as shown under APPARATUS. Missing sieves may result in bimodal or skewed particle size distribution. The following table provides an indication of the required sieve sizes:

<u>SAMPLE</u>	<u>SIEVE SIZES</u>
-1/4"	3 to 65
-20 mesh	10 to 100
-65 mesh	65 to 200

Should a large fraction appear either on the largest screen or the pan, additional sieves are needed.

NOTE 3: Sieve size should indicate a range, such as -3 + 4; -14 + 20; or -100 + 150.

## CALCULATIONS:

$$\text{Shale moisture, wt\%} = 100\% \times \frac{(W-1) - (W-2)}{(W-1) - (W-3)}$$



CALCULATIONS:

1. Determine the weight of shale on each sieve and pan.
2. Add the weights of shale together to determine the total (total weight (T)).
3. Determine the percent of shale on each sieve and pan by  
 $\% \text{ size (NOTE 2)} = 100 \times \text{net wt (gm)} / \text{T (gm)}$
4. Determine the overall recovery by:  
 $\% \text{ recovery} = 100 \times F \text{ (gm)} / \text{sample wt (gm)}$

NOTE 1: Proper sample size depends upon the mesh size of the sample being measured. For the types of samples normally analyzed in the laboratory the proper sample sizes are:  
 crushed shale (-1/4"), 500 gm; Fischer Assay (-20 mesh), 150 gm; "fine grind" (-65 mesh), 100 gm.

NOTE 2: In order to obtain normal distribution, the sieves should be arranged in numerical sequence (as shown under APPARATUS). Missing sieves may result in bimodal or skewed particle size distribution. The following table provides an indication of the required sieve sizes:

<u>SAMPLE</u>	<u>SIEVE SIZES</u>
-1/4"	3 to 65
-20 mesh	10 to 100
-65 mesh	65 to 200

Should a large fraction appear either on the largest screen or the pan, additional sieves are needed.

NOTE 3: Sieve size should indicate a range, such as -3 + 4; -14 + 20; or -100 + 150.

# PARAHO OIL SHALE DEMONSTRATION

## Raw Shale Moisture

### Method P-S-09

#### SCOPE:

This method determines the moisture on shale as fed to the retort. A grab sample of raw shale feed is analyzed for moisture.

#### OUTLINE OF METHOD:

A large sample (2000 gm) of raw shale ( $\frac{1}{2}$ " to 2") is dried at 105°C for 20 hours. The entire sample, received in a sealed metal can is used.

#### APPARATUS:

1. Gallon can with tight fitting cover.
2. Oven, 105°C
3. Balance, 5000 gm capacity

#### PROCEDURE:

1. Remove cover from sample can, weigh can and contents to nearest 0.1 gm (W-1)
2. Place in 105°C oven for 20 hours.
3. Weigh can and contents to nearest 0.1 gm (W-2)
4. Dump sample and weigh empty can to nearest 0.1 gm (W-3)

#### CALCULATIONS:

$$\text{Shale moisture, wt\%} = 100\% \times \frac{(W-1) - (W-2)}{(W-1) - (W-3)}$$



# PARADO OIL SHALE DEMONSTRATION

## Raw Shale Moisture

### Method P-2-02

#### SCOPE:

This method determines the moisture on shale as fed to the retort. A grab sample of raw shale feed is analyzed for moisture.

#### OUTLINE OF METHOD:

A large sample (1000 gm) of raw shale (± 2%) is dried at 105°C for 10 hours. The entire sample, received in a sealed metal can is used.

#### APPARATUS:

1. Galion can with tight fitting cover.
2. Oven, 105°C
3. Balance, 5000 gm capacity

#### PROCEDURE:

1. Remove cover from sample can, weigh can and contents to nearest 0.1 gm (W-1)
2. Place in 105°C oven for 10 hours.
3. Weigh can and contents to nearest 0.1 gm (W-2)
4. Dump sample and weigh empty can to nearest 0.1 gm (W-3)

#### CALCULATIONS:

$$\text{Shale moisture, \%} = 100 \times \frac{(W-1) - (W-2)}{(W-1) - (W-3)}$$

## TOTAL SULFUR

Method P-S-10

SCOPE:

The LECO high frequency combustion titration procedure is suitable for the analysis of sulfur in raw and retorted shales at levels greater than 0.05% sulfur. The complete determination takes less than ten minutes.

OUTLINE OF METHOD:

The sample is burned in an oxygen stream at a temperature sufficiently high to convert 90 to 97 percent of the sulfur to sulfur dioxide. The sulfur dioxide is carried by an oxygen stream to a titration cell containing an acid solution of potassium iodide and starch indicator and titrated with potassium iodate. A standardization factor is used to calculate the actual percent sulfur present.

APPARATUS:

1. Induction Furnace
2. Automatic Sulfur Titrator
3. 516-000 Purifying Train
4. 528-016 Combustion Crucibles
5. 528-042 Crucible Covers
6. 503-031 Loading Funnel
7. 503-032 Accelerator Scoop
8. 533-100 Starch Dispensor
9. 593-100 Timer

REAGENTS:

1. Magnesium Oxide, A.C.S. Reagent grade
2. Hydrochloric Acid. Dilute 15 ml of concentrated HCl to 1 liter with distilled water.
3. Tin Metal Accelerator, 501-076
4. Iron Powder Accelerator, 501-078
5. Oxygen USP
6. Potassium Iodate. Dissolve 0.44 gm of  $KIO_3$  in 1.0 liter of distilled, deionized water.
7. Starch - Iodide. Prepare slurry of 4 gm of starch in 100 ml of distilled, deionized water. Avoid using water stored in plastic vessels. Add the slurry slowly, while stirring, to 300 ml of boiling distilled, deionized water. Boil the solution for two minutes and cool to



## TOTAL SULFUR

Method P-2-10

## SCOPE:

The LECO high frequency combustion titration procedure is suitable for the analysis of sulfur in raw and retorted shales at levels greater than 0.05% sulfur. The complete determination takes less than ten minutes.

## OUTLINE OF METHOD:

The sample is burned in an oxygen stream at a temperature sufficiently high to convert 90 to 95 percent of the sulfur to sulfur dioxide. The sulfur dioxide is carried by an oxygen stream to a titration cell containing an acid solution of potassium iodide and starch indicator and titrated with potassium iodate. A standardization factor is used to calculate the actual percent sulfur present.

## APPARATUS:

1. Induction Furnace
2. Automatic Sulfur Titrator
3. 515-000 Purifying Train
4. 515-015 Combustion Chamber
5. 515-041 Crucible Covers
6. 503-031 Loading Funnel
7. 503-032 Accelerator Scoop
8. 513-100 Glass Dispenser
9. 503-100 Timer

## REAGENTS:

1. Magnesium Oxide, A.C.S. Reagent grade
2. Hydrochloric Acid, Dilute 12 ml of concentrated HCl in 1 liter with distilled water.
3. The Metal Accelerator, 501-075
4. Iron Powder Accelerator, 501-076
5. Oxygen USP
6. Potassium Iodate, Dissolve 0.44 gm of KIO<sub>3</sub> in 1.0 liter of distilled, deionized water.
7. Starch - 1% w/v. Prepare slurry of 1 gm of starch in 100 ml of distilled, deionized water. Avoid using water stored in plastic vessels. Add the slurry slowly, while stirring, to 500 ml of boiling distilled, deionized water. Boil the solution for two minutes and cool to

room temperature. When cool, dissolve, 12 gm of potassium iodide in the solution.

#### PROCEDURE:

##### A. Blank Determination

Add four level scoops of MgO (about 1.0 gm), two level scoops of low sulfur iron powder (about 1.25 gm), add one level scoop of tin granules (about 0.6 gm) to the combustion crucible. Place a porous crucible cover over the contents and burn them in the furnace. Record the percent sulfur observed on the buret. Average the readings for at least two determinations.

##### B. Determination of the Furnace Constant

Place two level scoops of MgO in combustion crucible. Make a small depression in the MgO and weigh 0.2 to 0.3 gm of LECO hydrocarbon standard into the crucible. Cover the sample with two level scoops of MgO, two level scoops of iron powder, and one level scoop of tin granules. Combust the sample and record the buret reading. Calculate the furnace constant as follows:

$$F = \frac{(S)(W)}{(T-B)}$$

Where F = Furnace constant

T = Buret titre as %S

B = Blank value as %S

S = Weight percent sulfur in standard

W = Weight of standard in grams

##### C. Sample Analysis

The same crucible is filled in the same manner as for the furnace constant calculation, except use the sample in place of the hydrocarbon standard. Use about 0.25 gm for liquids and about 0.2 gm for solids.

A. Insure all bubbles are out of the titration tubing.

B. Set oxygen flow to 1 liter/min.

Caution: Keep below 10 psig.



room temperature. When cool, dissolve, 12 gm of potassium iodide in the solution.

PROCEDURE:

A. Blank Determination

Add four level scoops of MgO (about 1.0 gm), two level scoops of low sulfur iron powder (about 1.25 gm), add one level scoop of tin granules (about 0.6 gm) to the combustion crucible. Place a porous crucible cover over the contents and burn them in the furnace. Record the percent sulfur observed on the buret. Average the readings for at least two determinations.

B. Determination of the Furnace Constant

Place two level scoops of MgO in combustion crucible. Make a small depression in the MgO and weigh 0.2 to 0.3 gm of 1500 hydrocarbon standard into the crucible. Cover the sample with two level scoops of MgO, two level scoops of iron powder, and one level scoop of tin granules. Combust the sample and record the buret reading. Calculate the furnace constant as follows:

$$F = \frac{(S)(W)}{(T-S)}$$

Where F = furnace constant  
T = buret titre as %  
S = blank value as %  
W = weight percent sulfur in standard  
W = weight of standard in grams

C. Sample Analysis

The same crucible is filled in the same manner as for the furnace constant calculation, except use the sample in place of the hydrocarbon standard. Use about 0.25 gm for liquids and about 0.3 gm for solids.

- A. Insert all bobbles are out of the titration reading.
- B. Set oxygen flow to 1 liter/min.
- Cautions: Keep below 10 psi.

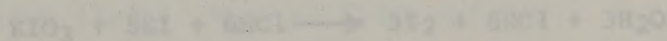
- C. Preheat ignitor for 45 seconds.
- D. Drain material in titration vessel and rinse once.
- E. Refill vessel about 1/2 full. Fill to same point each time, and bubble  $O_2$  through vessel.
- F. Add one charge of starch solution. Allow 1/2 min. to mix.
- G. Insure buret is full. Then turn double throw switch to "end point" position, and allow blue color to stabilize.
- H. Place crucible on pedestal and raise to locked position and refill buret
- I. Turn on timer and push red button (About 10 min. time is sufficient).
- J. When timer turns furnace off, drop pedestal and quickly remove crucible, check to be sure there is a good burn.
- K. Turn off titrator and read and record buret.

#### CALCULATIONS

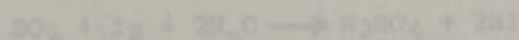
$$\%S = \frac{(F) (T-B)}{W}$$

- F = Furnace constant  
 T = Buret reading  
 B = Blank value  
 W = Sample weight in grams

The reactions in the titration vessel is as follows:



When sulfur dioxide is introduced the following reaction occurs:



Then the titration restores the original solution.



- C. Preheat ignitor for 45 seconds.
- D. Drain material in filtration vessel and rinse once.
- E. Refill vessel about 1/2 full. Fill to same point each time, and bubble  $O_2$  through vessel.
- F. Add one charge of starch solution. Allow 1/2 min. to mix.
- G. Increase burner to full. When turn double throw switch to "end point" position, and allow time to stabilize.
- H. Place crucible on pedestal and raise to locked position and refill buret.
- I. Turn on timer and push red button (about 10 min. time is sufficient).
- J. When timer turns furnace off, drop pedestal and quickly remove crucible, check to be sure there is a good burn.
- K. Turn off stirrer and read and record buret.

CALCULATIONS

$$\% S = \frac{W(T-S)}{W}$$

- F = Furnace constant  
 T = Buret reading  
 S = Blank value  
 W = Sample weight in grams

## APPENDIX

### LECO Sulfur Model 521 Induction Furnace

1. To energize Induction Furnace see Figure 10 on page 18 of Induction Furnace handbook.

2. Sometimes to start furnace it is necessary to turn on the Ignitor Switch.

3. Turn clock off while testing.

4. Read page 22 for proper crucible placement.

### LECO Sulfur Model 532 Titrator

1. Read pages 9-10 "Operating Procedure for Model 532-000"

2. End point determination is done at the start of each day's analyses. Place the end point knob in the far left position and the double-throw switch in the endpoint position. Rotate the end point knob until a medium blue color is attained in the titration vessel. No further adjustments are needed.

### Overnight Shutdown

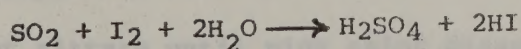
1. Turn off filament and high voltage switches.
2. Turn off titrator
3. Refill buret
4. Drain and refill titration vessel
5. Turn off oxygen
6. Turn off main power switch
7. Clean up area

### Reactions

The reactions in the titration vessel is as follows:



When sulfur dioxide is introduced the following reaction occurs:



Then the titration restores the original solution.



# APPENDIX

## LECO Sulfox Model 531 Induction Furnace

1. To analyze Induction Furnace see Figure 10 on page 18 of Induction Furnace Handbook.
2. Sometimes to start furnace it is necessary to turn on the Ignitor Switch.
3. Turn clock off while testing.
4. Read page 22 for proper crucible placement.

## LECO Sulfox Model 532 Titrator

1. Read pages 2-10 "Operating Procedures for Model 532-000".
2. End point determination is done at the start of each day's analysis. Place the end point knob in the far left position and the double-throw switch in the end point position. Rotate the end point knob until a medium blue color is obtained in the titration vessel. No further adjustments are needed.

## Overnight Shutdown

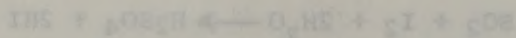
1. Turn off filament and high voltage switches.
2. Turn off titrator.
3. Refill buret.
4. Drain and refill titration vessel.
5. Turn off oxygen.
6. Turn off main power switch.
7. Clean up area.

## Reactions

The reactions in the titration vessel is as follows:



When sulfur dioxide is introduced the following reaction occurs:



Then the titration restores the original solution.

# PARAHO OIL SHALE DEMONSTRATION

CALCULATIONS:

Free Lime (CaO) = 0. Free Lime in Retorted Shale

Method P-S-11

## SCOPE:

This method determines free lime (CaO) in retorted shales using non-aqueous titrimetry. Other basic oxides, such as magnesia (MgO) do not interfere.

## PROCEDURE:

The method follows the procedure of ASTM C-114. The basic free lime, liberated by refluxing in a glycerol-alcohol solution, is titrated with ammonium acetate.

## APPARATUS:

1. Reflux apparatus with water-jacketed condenser.
2. Titration apparatus with titrant protected from contact with air.

## REAGENTS:

1. Solvent. Anhydrous glycerol: absolute ethanol, 1:5 (v:v); add about 0.2 gm phenolphthalein/1 liter. Then add alcoholic sodium hydroxide dropwise to a faint pink color.
2. Titrant. Dissolve 16 gm of dried ammonium acetate in 1 liter absolute ethanol. Protect from contact with air. Standardize against freshly prepared CaO.

## PROCEDURE:

1. Weigh sample in sealed vial (Since free lime can react with CO<sub>2</sub> or H<sub>2</sub>O, it should be protected from excessive contact with air).
2. Quickly transfer sample into 60-80 ml of solvent in a stoppered Erlenmeyer flask. Stopper flask quickly.
3. Reweigh empty vial.
4. Reflux sample for about 30 minutes.
5. While hot, titrate until pink color disappears.
6. Repeat steps 4 and 5 until no pink color reappears on refluxing.



# TARAHU OIL SHALE DEMONSTRATION

Free lime in Retorted Shale

Method 5-2-11

## SCOPE:

This method determines free lime (CaO) in retorted shales using non-  
aqueous titrimetry. Other basic oxides, such as magnesia (MgO) do not  
interfere.

## PROCEDURE:

The method follows the procedure of ASTM C-114. The basic free lime,  
liberated by refluxing in a glycerol-alcohol solution, is titrated with  
ammonium acetate.

## APPARATUS:

1. Reflux apparatus with water-jacketed condenser.
2. Titration apparatus with titrant protected from contact with air.

## REAGENTS:

1. Solvent. Anhydrous glycerol: absolute ethanol, 1:2 (v:v); add  
about 0.1 gm phenolphthalein/liter. Then add alcoholic sodium  
hydroxide dropwise to a faint pink color.
2. Titrant. Dissolve 10 gm of dried ammonium acetate in 1 liter  
absolute ethanol. Protect from contact with air. Standardize  
against freshly prepared CaO.

## PROCEDURE:

1. Weigh sample in sealed vial (Since free lime can react with CO<sub>2</sub> or  
H<sub>2</sub>O, it should be protected from excessive contact with air).
2. Quickly transfer sample into 60-80 ml of solvent in a stoppered  
Erlenmeyer flask. Stopper flask quickly.
3. Re-weigh empty vial.
4. Reflux sample for about 30 minutes.
5. While hot titrate until pink color disappears.
6. Repeat steps 4 and 5 until no pink color appears on refluxing.

CALCULATIONS:

$$\% \text{ Free Line (CaO)} = 0.65 \times \frac{\text{ml titrant}}{\text{gm sample}}$$

Method P-3-31

SCOPE:

The gravity, °API at 60°F, is determined on shale oils using hydrometers as described in ASTM D-267.

OUTLINE:

The shale oil, prepared by P-3-04, is transferred to the API bath. The hydrometer reading of the shale oil is converted to °API at 60°F using a table (1) and the temperature.

EQUIPMENT:

1. Series of API hydrometers
2. API Bath, 130°F
3. Thermometer, ASTM 197

PROCEDURE:

1. Fill a sample holder in the API bath with warm (130°F oil).
2. Record temperature of sample to nearest °F.
3. Place an appropriate hydrometer in the oil; make certain it is floating freely.
4. Record gravity to nearest 0.1° API and drain sample back to bottle.

CALCULATIONS:

Using the temperature of the oil and the hydrometer reading, determine the °API at 60°F from the table.

Report to nearest 0.1° API on report sheet P-1-1.

PRECISION:

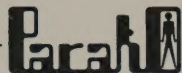
Duplicate results should agree within 0.1° API.

(1) ASTM-IP Petroleum Measurement Tables



CALCULATIONS:

$$I \text{ Free Line (CaO)} = 0.62 \times \frac{\text{ml titrant}}{\text{gm sample}}$$



## PARAHO OIL SHALE DEMONSTRATION

### API Gravity

#### Method P-O-01

#### SCOPE:

The gravity, °API at 60°, is determined on shale oils using hydrometers as described in ASTM D-287.

#### OUTLINE:

The shale oil, prepared by P-P-04, is transferred to the API bath. The hydrometer reading of the clean oil is converted to °API at 60°F using a table (1) and the temperature.

#### EQUIPMENT:

1. Series of API hydrometers
2. API Bath, 130°F
3. Thermometer, ASTM 19F

#### PROCEDURE:

1. Fill a sample holder in the API bath with warm (140°F oil).
2. Record temperature of sample to nearest °F.
3. Place an appropriate hydrometer in the oil; make certain it is floating freely.
4. Record gravity to nearest 0.1° API and drain sample back to bottle.

#### CALCULATIONS:

Using the temperature of the oil and the hydrometer reading, determine the °API at 60°F from the table.

Report to nearest 0.1° API on report sheet P-L-1.

#### PRECISION:

Duplicate results should agree within 0.3° API.

- (1) ASTM-IP Petroleum Measurement Tables



# PARAFFIN OIL SHALE DEMONSTRATION

API Gravity

Method T-0-01

## SCOPE:

The gravity, °API at 60°, is determined on shale oils using hydrometers as described in ASTM D-287.

## OUTLINE:

The shale oil, prepared by P-9-04, is transferred to the API bath. The hydrometer reading of the clean oil is converted to °API at 60°F using a table (1) and the temperature.

## EQUIPMENT:

1. Series of API hydrometers
2. API bath, 140°F
3. Hydrometer, ASTM 197

## PROCEDURE:

1. Fill a sample holder in the API bath with warm (140°F oil).
2. Record temperature of sample to nearest °F.
3. Place an appropriate hydrometer in the oil; make certain it is floating freely.
4. Record gravity to nearest 0.1° API and drain sample back to bottle.

## CALCULATIONS:

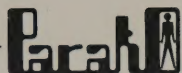
Using the temperature of the oil and the hydrometer reading, determine the °API at 60°F from the table.

Report to nearest 0.1° API on report sheet P-1-1.

## PRECISION:

Duplicate results should agree within 0.3° API.

(1) ASTM-15 Petroleum Measurement Tables



## PARAHO OIL SHALE DEMONSTRATION

### Saybolt Viscosity

#### Method P-O-02

#### SCOPE:

This method determines the viscosity of shale oil at two temperatures using the Saybolt viscometer as described in ASTM D-88.

#### OUTLINE:

The time required for a definite volume of shale oil to flow through a fixed orifice is measured. The oil is heated to 130°F or 210°F.

#### EQUIPMENT:

1. Saybolt Viscometers, one at 130°F, one at 210°F.
2. Funnels with 100-mesh screen.
3. Thermometers, ASTM 19F and 22F.
4. Receiving Flasks.

#### PROCEDURE:

1. Pass sufficient shale oil through a 100 mesh filter to fill the viscometer to the overflow rim.
2. Allow the oil to attain the proper temperature (130°F or 210°F) then remove the thermometer. Residence time should not exceed one hour.
3. Check to be certain that the oil level is even with the brass ring of the reservoir. Remove excess oil from the gallery with a pipet or dropper.
4. Pull the cork stopper allowing the oil to drain through the orifice into the receiving flask. At the same time, start the stop-watch timer.
5. When the level reaches the 60 ml mark, stop the stop-watch.
6. Clean the reservoir gallery and orifice with toluene. Swab with Kim-Wipe.

#### CALCULATIONS:

Viscosity, \_\_\_\_\_ °F, SUS = seconds noted on stop-watch.

#### PRECISION:

Duplicate results should agree within 14. SUS (210°F) or 2 SUS (130°F).



# PARAFFIN OIL SEALS DEMONSTRATION

## Saybolt Viscosity

Method P-O-93

### SCOPE:

This method determines the viscosity of shale oil at two temperatures using the Saybolt viscometer as described in ASTM D-88.

### OUTLINE:

The time required for a definite volume of shale oil to flow through a fixed orifice is measured. The oil is heated to 130°F or 210°F.

### EQUIPMENT:

1. Saybolt Viscometer, one at 130°F, one at 210°F.
2. Funnel with 100-mesh screen.
3. Thermometer, ASTM 19F and 21F.
4. Receiving Flasks.

### PROCEDURE:

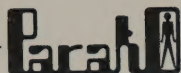
1. Pass sufficient shale oil through a 100 mesh filter to fill the viscometer to the overflow rim.
2. Allow the oil to attain the proper temperature (130°F or 210°F) then remove the thermometer. Resistance time should not exceed one hour.
3. Check to be certain that the oil level is even with the brass ring of the reservoir. Remove excess oil from the gallery with a pipet or dropper.
4. Pull the cork stopper allowing the oil to drain through the orifice into the receiving flask.
5. At the same time, start the stop-watch timer.
6. When the level reaches the 60 ml mark, stop the stop-watch.
7. Clean the reservoir gallery and orifice with toluene. Wash with kerosene.

### CAUTIONS:

Viscosity, \_\_\_\_\_, SUS = seconds noted on stop-watch.

### REMARKS:

Repetitive results should agree within 1% SUS (210°F) or 2 SUS (130°F).



## PARAHO OIL SHALE DEMONSTRATION

### Water in Oil Product

#### Method P-O-03

#### SCOPE:

Water, in concentrations greater than 0.2 wt%, is determined in the oil product as described in ASTM D-95.

#### OUTLINE OF METHOD:

Toluene is heated with the sample. Water distills with the toluene. The distilled toluene drains back to the flask while the water separates out and is measured in a calibrated Dean-Stark trap.

#### EQUIPMENT:

1. Heater.
2. Round-bottom flask, 500 ml, 24/40 S.
3. Dean-Stark flask, 10 ml capacity, 24/40 S.
4. Liebig Condenser 24/40 S.

#### REAGENTS:

1. Toluene

#### PROCEDURE:

1. Weigh 50-100 gm of oil product into tared flask.
2. Add 100 ml of toluene and a few boiling stones.
3. Assemble apparatus, heat to boiling (2-5 drops/second). Check flow through condenser.
4. Continue boiling until no difference in the water collected in the trap is noted in a 15 minute period.
5. Allow the apparatus to cool and read the water volume.
6. Discard the flask contents into a solvent can. Rinse apparatus with acetone.

#### CALCULATIONS:

$$\text{Water (wt\%)} = \frac{\text{ml. of water in trap}}{\text{Wt. of sample (gm)}} \times 100\%$$

Report water in oil to nearest 0.01 wt% on report sheet P-L-1.

#### PRECISION:

Duplicate results should agree within 0.1 wt%



# ASTM D-92

Water in Oil Product

Method D-92

## SCOPE

Water, in concentrations greater than 0.1 wt%, is determined in the oil product as described in ASTM D-92.

## OUTLINE OF METHOD

Toluene is heated with the sample. Water distills with the toluene. The distilled toluene drains back to the flask while the water separates out and is measured in a calibrated Dean-Stark trap.

## EQUIPMENT

1. Heater.
2. Round-bottom flask, 500 ml, 24/40 S.
3. Dean-Stark trap, 10 ml capacity, 24/40 S.
4. Liebig Condenser 24/40 S.

## REAGENTS

1. Toluene

## PROCEDURE

1. Weigh 50-100 gm of oil product into tared flask.
2. Add 100 ml of toluene and a few boiling stones.
3. Assemble apparatus, heat to boiling (2-3 drops/second). Check flow through condenser.
4. Continue boiling until no difference in the water collected in the trap is noted in a 15 minute period.
5. Allow the apparatus to cool and read the water volume.
6. Discard the flask contents into a solvent can. Rinse apparatus with acetone.

## CALCULATIONS

$$\text{Water (wt\%)} = \frac{\text{ml. of water in trap}}{\text{Wt. of sample (gm)}} \times 100\%$$

Report water in oil to nearest 0.01 wt% on report sheet P-1-1.

## PRECISION

Duplicate results should agree within 0.1 wt%



## PARAHO OIL SHALE DEMONSTRATION

### Ramsbottom Carbon

#### Method P-O-04

#### SCOPE:

This method is designed to measure the Ramsbottom Carbon residue as described in ASTM D-524.

#### OUTLINE:

A weighed sample of shale oil is heated in a tared Ramsbottom coking bulb for a specified time. The coke remaining is a measure of the Ramsbottom Carbon.

#### EQUIPMENT:

1. Ramsbottom Furnace, maintained at  $1020 \pm 10^{\circ}\text{F}$ .
2. Ramsbottom Coking Bulbs.
3. Hypodermic Syringe, 5 ml with 20 gauge needles.

#### PROCEDURE:

1. Using a hypodermic syringe, add 1.5 gm (or less) of clean, filtered shale oil into a coking bulb that had been tared to the nearest 0.1 mg. Make sure that no oil is in the neck of the coking bulb. Convenient source of sample is drain from viscosity measurement.
2. Weigh the bulb + oil to nearest 0.1 mg to determine the sample weight.
3. Place into well in Ramsbottom furnace (maintained at  $1020 \pm 10^{\circ}\text{F}$ ) for  $20 \pm 2$  min. If flaming or sputtering occurs, test must be rerun.
4. Remove the bulb and allow to cool in a dessicator for 1 hour.
5. Reweigh to nearest 0.1 mg to determine coke residue.

#### CALCULATIONS:

$$\text{Wt \% Ramsbottom Carbon} = 100\% \times \frac{\text{Wt of coke residue (gms)}}{\text{Wt of sample (gms)}}$$

Report Ramsbottom C to nearest 0.01 wt% on report sheet P-L-1.

#### PRECISION:

Duplicate results should agree within 0.4%.



# PARANO OIL SHALE DEMONSTRATION

Ramsbottom Carbon

Method P-O-04

## SCOPE:

This method is designed to measure the Ramsbottom Carbon residue as described in ASTM D-524.

## OUTLINE:

A weighed sample of shale oil is heated in a tarred Ramsbottom coking bulb for a specified time. The coke remaining is a measure of the Ramsbottom Carbon.

## EQUIPMENT:

1. Ramsbottom Furnace, maintained at  $1020 \pm 10^\circ\text{F}$ .
2. Ramsbottom Coking Bulb.
3. Hypodermic Syringe, 5 ml with 30 gauge needles.

## PROCEDURE:

1. Using a hypodermic syringe, add 1.5 gm (or less) of clean, filtered shale oil into a coking bulb that had been tarred to the nearest 0.1 mg. Make sure that no oil is in the neck of the coking bulb. Convenient source of sample is drain from viscosity measurement.
2. Weigh the bulb + oil to nearest 0.1 mg to determine the sample weight.
3. Place bulb well in Ramsbottom Furnace (maintained at  $1020 \pm 10^\circ\text{F}$ ) for 30  $\pm$  5 min. If flaming or spattering occurs, test must be rerun.
4. Remove the bulb and allow to cool in a desiccator for 1 hour.
5. Reweigh to nearest 0.1 mg to determine coke residue.

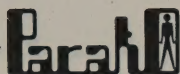
## CALCULATIONS:

$$\text{Rt \& Ramsbottom Carbon} = 100 \times \frac{\text{Wt of coke residue (gms)}}{\text{Wt of sample (gms)}}$$

Report Ramsbottom C to nearest 0.01 wt% on report sheet P-L-1.

## PRECISION:

Duplicate results should agree within 0.4%.



## PARAHO OIL SHALE DEMONSTRATION

### Sediment in Oil-Centrifuge Method

(Total) Method No. P-O-05 and Nitrogen

Method P-O-05

#### SCOPE:

This method determines the sediment in oil by separation using centrifuging. Although the method could also be used for determining water, azeotropic distillation (Method P-O-04) is recommended because it is more reliable. Sediment is reported in vol/wt% (ml of sediment/100 gm of oil sample).

#### OUTLINE:

A small amount of water is added to a weighed sample of oil. After heating, the sample is centrifuged and the volume of sediment is measured.

#### EQUIPMENT:

1. Water bath, 80°C.
2. Centrifuge Tubes, 100-ml, pear shape; stem graduated 0-3 ml.
3. Centrifuge.

#### PROCEDURE:

1. Weigh about 50 gm to nearest 0.01 gm in tared centrifuge tube.
2. Add 1 ml of water and place in 80°C bath for 10 minutes.
3. Centrifuge at 2000 RPM for 10 minutes.
4. Measure the volume of sediment to the nearest 0.1 ml.

#### CALCULATIONS:

Sediment (vol/wt%) = 100% x ml sediment/gm sample.

Report sediment to nearest 0.01 vol/wt% on report sheet P-L-1.

#### PRECISION:

Duplicate results should agree within 0.5 wt%.



# PARAFFIN OIL SHALE DEMONSTRATION

## Sediment in Oil-Centrifuge Method

Method No. P-O-02

### SCOPE:

This method determines the sediment in oil by separation using centrifuging. Although the method could also be used for determining water, azeotropic distillation (Method P-O-04) is recommended because it is more reliable. Sediment is reported in vol/vol (ml of sediment/100 gm of oil sample).

### OUTLINE:

A small amount of water is added to a weighed sample of oil. After heating, the sample is centrifuged and the volume of sediment is measured.

### EQUIPMENT:

1. Water bath, 80°C.
2. Centrifuge Tubes, 100-ml, pear shape; stem graduated 0-1 ml.
3. Centrifuge.

### PROCEDURE:

1. Weigh about 50 gm to nearest 0.01 gm in tared centrifuge tube.
2. Add 1 ml of water and place in 80°C bath for 10 minutes.
3. Centrifuge at 3000 RPM for 10 minutes.
4. Measure the volume of sediment to the nearest 0.1 ml.

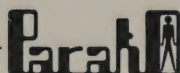
### CALCULATIONS:

Sediment (vol/vol) =  $100 \times \text{ml sediment} / \text{gm sample}$

Report sediment to nearest 0.01 vol/vol on report sheet P-I-1.

### PRECISION:

Duplicate results should agree within 0.2 wt%.



## PARAHO OIL SHALE DEMONSTRATION

### Elemental Analysis

(Total Carbon, Hydrogen, and Nitrogen)

Method P-0-06

#### SCOPE:

This method determines the total carbon, hydrogen, and nitrogen in shale oil. Comparison with other laboratories and repeatability of the analyses are usually less than 0.2 wt%.

#### OUTLINE:

This method is the same as P-S-05 except that the sample is reduced to 1-2 mg and is encapsulated to prevent volatility losses.

#### EQUIPMENT:

The equipment is the same as P-S-05 with the addition of:

1. Sample pans and covers, PE 219-0062.
2. Volatile sample sealer, PE 219-061.

#### PROCEDURE:

The procedure is the same as P-S-05 except for section G, 1:

- a. Use 1-2 mg of oil.
- b. Encapsulate sample in pan and cover before combustion.
- c. No oxygen donors or other oxidization aids are needed.

3. Increase heat, record  $\bar{V}$  at 5 ml, 10 ml (and subsequent 10 ml intervals) until cracking temperature (indicated by a sharp drop in temperature). Record highest temperature and final volume collected in the receiver.

4. Record the atmospheric pressure to nearest mm Hg.

5. Clean up apparatus while still warm.

#### CALCULATIONS:

Correction to 760 mm Hg -- ASTM D-92



BARBARO OIL SHALE DEMONSTRATION

Elemental Analysis

(Total Carbon, Hydrogen, and Nitrogen)

Method P-2-05

SCOPE:

This method determines the total carbon, hydrogen, and nitrogen in shale oil. Comparison with other laboratories and repeatability of the analyses are usually less than 0.2 wt%.

OUTLINE:

This method is the same as P-2-05 except that the sample is reduced to 1-2 mg and is encapsulated to prevent volatility losses.

EQUIPMENT:

The equipment is the same as P-2-05 with the addition of:

1. Sample pans and covers, PS 212-0082.
2. Volatile sample seals, PS 212-0081.

PROCEDURE:

The procedure is the same as P-2-05 except for section C. 1:

- a. Use 1-2 mg of oil.
- b. Encapsulate sample in pan and cover before combustion.
- c. No oxygen donors or other oxidation aids are needed.

## PARAHO OIL SHALE DEMONSTRATION

### Atmospheric Distillation

1. Factor = 0.00012 (7) Method P-O-07

#### SCOPE:

The distillation of shale oil is monitored from the initial boiling point until cracking is noticed. The method is a modification of ASTM D-86.

#### OUTLINE:

A measured volume of shale oil is heated electrically and the temperature of the initial point, 5 ml, 10 ml, (and subsequent 10 ml intervals) is noted.

#### APPARTUS:

1. ASTM Distillation Apparatus.
2. Thermometer, ASTM 8F.
3. Barometer.

#### PROCEDURE:

1. Swab out condenser to remove any foreign matter. Assemble the apparatus, having about 1-2 inches of cool water in the reservoir, 100 ml of clean shale oil in the distillation flask, the thermometer positioned properly (bulb just below the condenser joint and not touching the walls), and a clean 100 ml graduate as a receiver.
2. Heat the flask and oil slowly until the initial point (first distillate drops off the condenser). Record i.p. (°F).
3. Increase heat, record °F at 5 ml, 10 ml (and subsequent 10 ml intervals) until cracking temperature (indicated by a sharp drop in temperature). Record highest temperature and final volume collected in the receiver.
4. Record the atmospheric pressure to nearest mm Hg.
5. Clean up apparatus while still warm.

#### CALCULATIONS:

Correction to 760 mm Hg -- ASTM D-86



## Atmospheric Distillation

Method P-O-07

SCOPE:

The distillation of shale oil is monitored from the initial boiling point until cracking is noticed. The method is a modification of ASTM D-86.

OUTLINE:

A measured volume of shale oil is heated electrically and the temperature of the initial point, 5 ml, 10 ml, and subsequent 10 ml intervals is noted.

APPARATUS:

1. ASTM Distillation Apparatus.
2. Thermometer, ASTM B.
3. Barometer.

PROCEDURE:

1. Wash out condenser to remove any foreign matter. Assemble the apparatus, having about 1-2 inches of cool water in the reservoir, 100 ml of clean shale oil in the distillation flask, the thermometer positioned properly (bulb just below the condenser joint and not touching the walls), and a clean 100 ml graduate as a receiver.
2. Heat the flask and oil slowly until the initial point (first distillate drops off the condenser). Record t.p. (°F).
3. Increase heat, record °F at 5 ml, 10 ml and subsequent 10 ml intervals until cracking temperature (indicated by a sharp drop in temperature). Record highest temperature and final volume collected in the receiver.
4. Record the atmospheric pressure to nearest mm Hg.
5. Clean up apparatus while still warm.

CALCULATION:

Correction to 760 mm Hg — ASTM D-86

# PARAHO OIL SHALE DEMONSTRATION

$$1. \text{ Factor} = 0.00012 (760 - P) (460 + T)$$

where P = atmospheric press (mm Hg)

T = observed temperature ( $^{\circ}\text{F}$ )

$$2. \text{ Corrected Temp.} = T + \text{Factor}$$

Report corrected temperature for all fractions (i.p., 5 ml, 10 ml, 20 ml ... cracking temperature) on P-L-1.

## PRECISION:

No data available.

## EQUIPMENT:

1. Test jar.
2.  $105^{\circ}\text{F}$  oven.
3. Thermometer, ASTM 32.
4. Ice.

## PROCEDURE:

1. Pour about 50 ml of clean shale oil into a test jar and heat to  $105^{\circ}\text{F}$  in the oven.
2. Assemble the apparatus as shown in Figure 2-3. Use an ice-water solution to fill the bath (about a 700 ml solution in a 1000 ml beaker is suitable).
3. After the oil has cooled to about  $90^{\circ}\text{F}$ , check the pour point by removing the test jar, tilting slightly to note any movement, and replacing in the bath.
4. When no movement of the oil is detected, when the test jar is tilted in the horizontal position for 5 seconds, the experiment is stopped.

## CALCULATIONS:

Pour Point = (temperature at which no movement is detected)  $+ 5^{\circ}\text{F}$ .

Report pour point to nearest  $5^{\circ}\text{F}$  on report sheet P-L-1.



1. Factor =  $0.00012 (100 - T)$  (400 + T)

where T = atmospheric pressure (mm Hg)  
T = observed temperature (°F)

2. Corrected Temp. = T + Factor

Report corrected temperature for all fractions (i.e., 5 ml, 10 ml, 20 ml ... tracking temperature) on P-1-1.

PRECISION:

No data available.

## PARAHO OIL SHALE DEMONSTRATION

### Pour Point of Shale Oil

Method P-0-08

#### SCOPE:

The pour point, defined as the lowest temperature at which movement occurs, is determined by ASTM D-97.

#### OUTLINE:

Clean oil is heated to 105°F, then cooled until movement no longer occurs.

#### EQUIPMENT:

1. Test jar.
2. 105°F Oven.
3. Thermometer, ASTM 5F.
4. Ice.

#### PROCEDURE:

1. Pour about 50 ml of clean shale oil into a test jar and heat to 105°F in the oven.
2. Assemble the apparatus as shown in Figure 2-3. Use an ice water solution to fill the bath (about a 700 ml solution in a 1000 ml beaker is suitable).
3. After the oil has cooled to about 95°F, check the pour point by removing the test jar, tilting slightly to note any movement, and replacing in the bath.
4. When no movement of the oil is detected, when the test jar is tilted in the horizontal position for 5 seconds, the experiment is stopped.

#### CALCULATIONS:

Pour Point = (temperature at which no movement is detected)  
+ 5°F.

Report pour point to nearest 5°F on report sheet P-L-1.

Oil Sample

Ice Water

Pour Point Apparatus

Figure 2-3



# PARAFFIN OIL SHALE DEMONSTRATION

## Pour Point of Shale Oil

Method P-9-98

### SCOPE:

The pour point, defined as the lowest temperature at which movement occurs, is determined by ASTM D-97.

### OUTLINE:

Clean oil is heated to 105°F, then cooled until movement no longer occurs.

### EQUIPMENT:

1. Test Jar
2. 105°F Oven
3. Thermometer, ASTM 2F
4. Ice

### PROCEDURE:

1. Pour about 50 ml of clean shale oil into a test jar and heat to 105°F in the oven.
2. Assemble the apparatus as shown in Figure 2-3. Use an ice water solution to fill the bath (about a 700 ml solution in a 1000 ml beaker is suitable).
3. After the oil has cooled to about 95°F, check the pour point by removing the test jar, tilting slightly to note any movement, and replacing in the bath.
4. When no movement of the oil is detected, when the test jar is tilted in the horizontal position for 5 seconds, the experiment is stopped.

### CALCULATIONS:

Pour Point = (temperature at which no movement is detected) + 2°F.

Report pour point to nearest 5°F on report sheet P-1-1.

# PARAFFIN OIL SHALE DEMONSTRATION

Oil Shale and Oil

Method P-0-09

## SCOPE:

This procedure is modified from P-0-09. The final temperature has been raised to 950°C to convert the mineral carbonates to oxides.

## PROCEDURE:

A weighed sample of oil shale and the coke residue backed in a 950°C muffle furnace.

## EQUIPMENT:

1. Evaporating dish, 100-ml capacity
2. Burette
3. Hot plate or infrared lamp
4. Muffle furnace

## PROCEDURE:

1. Heat a dry, clean evaporating dish to 950°C for 10 minutes or more.
2. Cool in a desiccator for 1 hour and obtain a tare weight (to nearest 0.1 mg).
3. Weigh into the dish 10.0 g (to nearest 0.2 mg) of oil.
4. Warm the oil until bubbling can be maintained to a uniform, moderate rate.
5. When bubbling ceases, place the dish into a 950°C muffle furnace.
6. Heat for at least 30 minutes after the disappearance of the coke or carbonaceous material.
7. Remove carefully (the ash should be quite fluffy and light) and cool in a desiccator for 1 hour.
8. Transfer to the balance carefully and weigh to the nearest 0.1 mg.

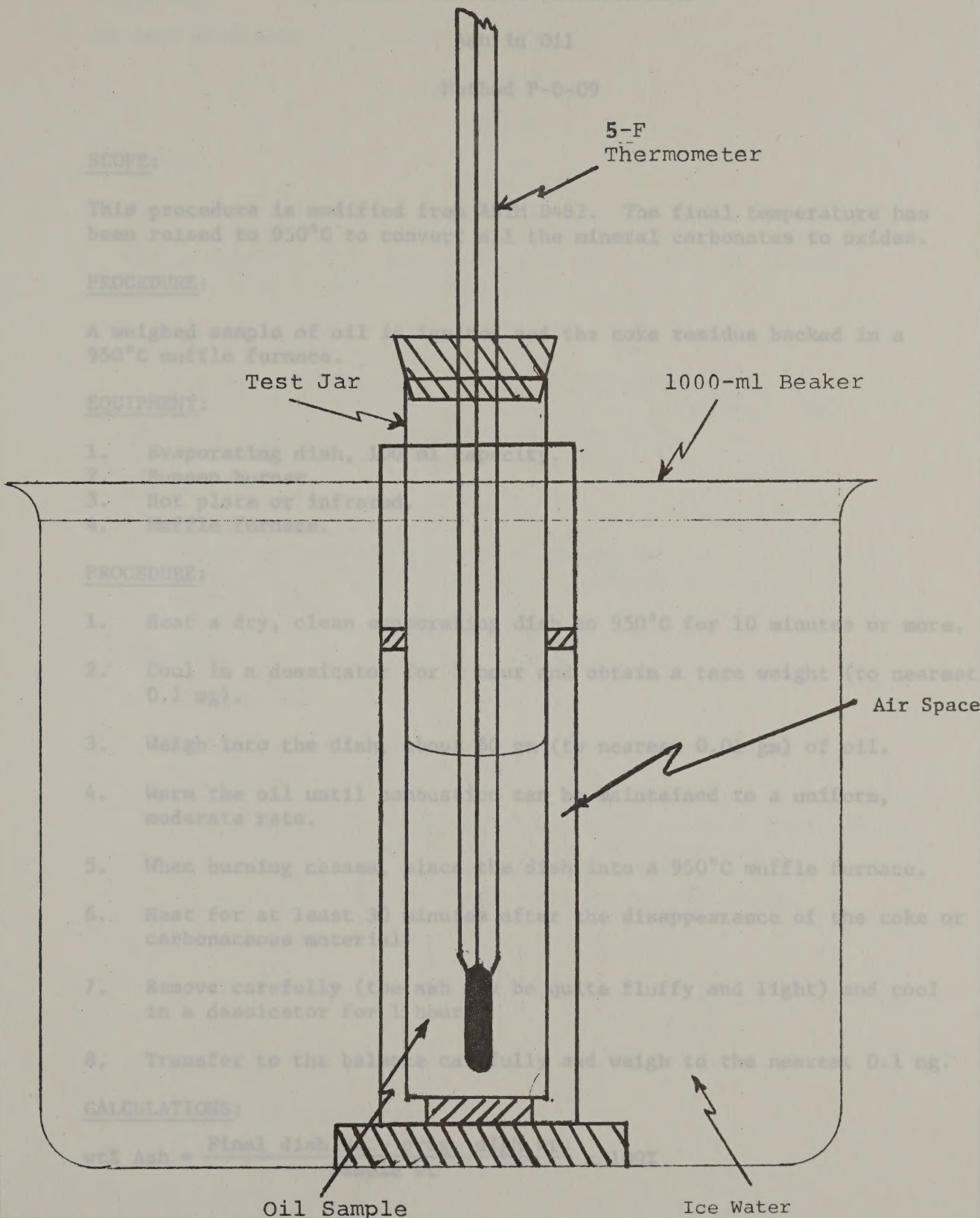
## CALCULATIONS:

wt% Ash =  $\frac{\text{Final dish} - \text{Tare}}{\text{Sample}}$

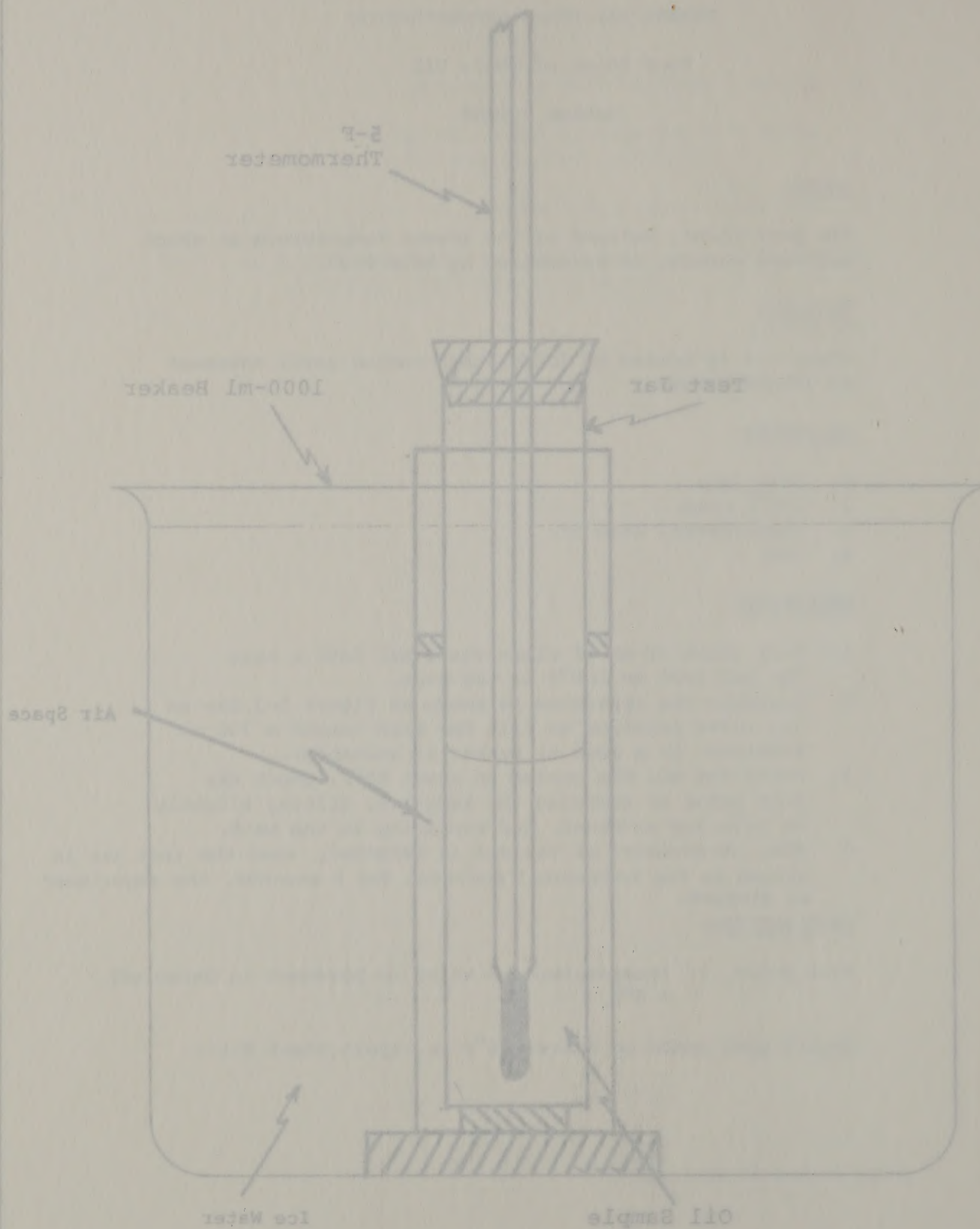
Report ash to nearest 0.01 wt% on report sheet P-0-09.

Pour Point Apparatus

Figure 2-3







Four Point Apparatus

Figure 2-3

PRECISION:

## PARAHO OIL SHALE DEMONSTRATION

No data available.

Ash in Oil

Method P-0-09

### SCOPE:

This procedure is modified from ASTM D482. The final temperature has been raised to 950°C to convert all the mineral carbonates to oxides.

### PROCEDURE:

A weighed sample of oil is ignited and the coke residue backed in a 950°C muffle furnace.

### EQUIPMENT:

1. Evaporating dish, 100 ml capacity.
2. Bunsen burner.
3. Hot plate or infrared.
4. Muffle furnace.

### PROCEDURE:

1. Heat a dry, clean evaporating dish to 950°C for 10 minutes or more.
2. Cool in a dessicator for 1 hour and obtain a tare weight (to nearest 0.1 mg).
3. Weigh into the dish, about 50 gm (to nearest 0.01 gm) of oil.
4. Warm the oil until combustion can be maintained to a uniform, moderate rate.
5. When burning ceases, place the dish into a 950°C muffle furnace.
6. Heat for at least 30 minutes after the disappearance of the coke or carbonaceous material.
7. Remove carefully (the ash may be quite fluffy and light) and cool in a dessicator for 1 hour.
8. Transfer to the balance carefully and weigh to the nearest 0.1 mg.

### CALCULATIONS:

$$\text{wt\% Ash} = \frac{\text{Final dish wt} - \text{orig. dish wt.}}{\text{Sample wt}} \times 100\%$$

Report ash to nearest 0.01 wt% on report sheet P-L-1.



# PARAFFIN OIL SHALE DEMONSTRATION

Ash in Oil

Method P-0-07

## SCOPE:

This procedure is modified from ASTM D482. The final temperature has been raised to 950°C to convert all the mineral carbonates to oxides.

## PROCEDURE:

A weighed sample of oil is ignited and the coke residue packed in a 950°C muffle furnace.

## EQUIPMENT:

1. Evaporating dish, 100 ml capacity.
2. Bunsen burner.
3. Hot plate or infrared.
4. Muffle furnace.

## PROCEDURE:

1. Heat a dry, clean evaporating dish to 950°C for 10 minutes or more.
2. Cool in a desiccator for 1 hour and obtain a tare weight (to nearest 0.1 mg).
3. Weigh into the dish, about 50 gm (to nearest 0.01 gm) of oil.
4. Warm the oil until combustion can be maintained to a uniform, moderate rate.
5. When burning ceases, place the dish into a 950°C muffle furnace.
6. Heat for at least 30 minutes after the disappearance of the coke or carbonaceous material.
7. Remove carefully (the ash may be quite flaky and light) and cool in a desiccator for 1 hour.
8. Transfer to the balance carefully and weigh to the nearest 0.1 mg.

## CALCULATIONS:

$$\text{wt Ash} = \frac{\text{Final dish wt} - \text{orig. dish wt.}}{\text{Sample wt}} \times 100\%$$

Report ash to nearest 0.01 wt% on report sheet P-0-1.

PRECISION:

No data available.

PARAHO OIL SHALE DEMONSTRATION

Pycnometer Gravity

Method P-O-10

SCOPE:

Pycnometers are used to measure the specific gravity of oils as an alternative to the hydrometer method (P-O-01). The pycnometer method is used to measure the gravity of Fincher assay oils or check hydrometer data.

OUTLINE:

A calibrated pycnometer is carefully filled with oil. The temperature is noted and the weight of oil calculated. The specific gravity is then corrected to 60/60°F.

EQUIPMENT:

1. Pycnometers, 2 ml.
2. Aluminum block with wells for pycnometers and thermometers.
3. Thermometer, capable of measuring ambient temperature to nearest 1°F.

PROCEDURE:

1. Calibration
  - a. Obtain bare weight of dry, clean pycnometer to nearest 0.1 mg and note.
  - b. Fill with deionized water, allow to stand in aluminum block at 66-73°F for an hour. Carefully insert capillary cap, dry the outer surface, and reweigh to nearest 0.1 mg. Note temperature and weight.
2. Determination
  - a. Fill pycnometer with dry oil as described in Calibration.
  - b.

CALCULATIONS:

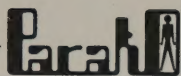
1. Volume of pycnometer

$$vt \text{ of water} = \frac{1 b - 1 a}{d \text{ at temp (1 b)}}$$



PRECISION:

No data available.



## PARAHO OIL SHALE DEMONSTRATION

### Pycnometer Gravity

#### Method P-O-10

#### SCOPE:

Pycnometers are used to measure the specific gravity of oils as an alternative to the hydrometer method (P-O-01). The pycnometer method is used to measure the gravity of Fischer assay oils or check hydrometer data.

#### OUTLINE:

A calibrated pycnometer is carefully filled with oil. The temperature is noted and the weight of oil calculated. The specific gravity is then corrected to 60/60°F.

#### EQUIPMENT:

1. Pycnometers, 2 ml.
2. Aluminum block with wells for pycnometers and thermometers.
3. Thermometer, capable of measuring ambient temperature to nearest 1°F.

#### PROCEDURE:

1. Calibration
  - a. Obtain tare weight of dry, clean pycnometer to nearest 0.1 mg and note.
  - b. Fill with deionized water, allow to stand in aluminum block at 66-73°F for an hour. Carefully insert capillary cap, dry the outer surface, and reweigh to nearest 0.1 mg. Note temperature and weight.
2. Determination
  - a. Fill pycnometer with dry oil as described in Calibration, b.

#### CALCULATIONS:

1. Volume of pycnometer

$$\text{wt of water} = 1 \text{ b} - 1 \text{ a at temp (1 b)}$$



# PARAFFIN OIL SHALE DEMONSTRATION

## Pycnometer Gravity

Method P-O-10

### SCOPE:

Pycnometers are used to measure the specific gravity of oils as an alternative to the hydrometer method (P-O-01). The pycnometer method is used to measure the gravity of viscous assay oils or check hydrometer data.

### OUTLINE:

A calibrated pycnometer is carefully filled with oil. The temperature is noted and the weight of oil calculated. The specific gravity is then corrected to 60/60°F.

### EQUIPMENT:

1. Pycnometer, 5 ml.
2. Aluminum block with wells for pycnometer and thermometer.
3. Thermometer, capable of measuring ambient temperature to nearest 0.1°F.

### PROCEDURE:

#### 1. Calibration

- a. Obtain tare weight of dry, clean pycnometer to nearest 0.1 mg and note.
- b. Fill with distilled water, allow to stand in aluminum block at 66-72°F for an hour. Carefully insert capillary cap, dry the outer surface, and reweigh to nearest 0.1 mg. Note temperature and weight.

#### 2. Determination

- a. Fill pycnometer with dry oil as described in Calibration.
- b.

### CALCULATIONS:

#### 1. Volume of pycnometer

wt of water =  $j \cdot b - i$  at temp (i, b)

$$\text{Vol (ml)} = \text{wt of water} \times F (t)$$

Temp.	F(t)
66	1.00153
67	1.00165
68	1.00177
69	1.00190
70	1.00201
71	1.00213
72	1.00226
73	1.00239

#### SCOPE:

This method determines sulfur in oil using the Leco Model Sulfur Analyzer. The method determines total sulfur at 200°C.

#### 2. Specific Gravity of Oil (T/60°)

$$2 a - 1 a$$

$$\text{Sp. Gr (T/60°)} = \frac{\text{Vol}}{\text{Vol}} \quad \text{at T( 2 b)}$$

3. Specific Gravity of Oil (60/60°F)   
 refer to the procedure or calculations.

$$\text{Sp. Gr. (60/60°F)} = \text{Sp. Gr (T/60°F)} - 0.0036$$

#### 4. Gravity (°API) of Oil

$$^{\circ}\text{API (60/60°F)} = \frac{141.5}{\text{Sp. Gr. (60/60°F)}} - 131.5$$



Vol (ml) = wt of water x F (2)

Temp. F (2)

66	1.00153
67	1.00163
68	1.00173
69	1.00180
70	1.00201
71	1.00213
72	1.00236
73	1.00259

2. Specific Gravity of Oil (T/60°)

$$\text{Sp. Gr. (T/60°)} = \frac{\text{Wt.} - \text{Wt. of water}}{\text{Vol}}$$

3. Specific Gravity of Oil (60/60°F)

$$\text{Sp. Gr. (60/60°F)} = \text{Sp. Gr. (T/60°F)} - 0.0036$$

4. Gravity (API) of Oil

$$\text{API (60/60°F)} = \frac{141.5}{\text{Sp. Gr. (60/60°F)}} - 131.5$$

# PARAHO OIL SHALE DEMONSTRATION

## Gas Chromatographic Analysis of Product Gas

### PARAHO OIL SHALE DEMONSTRATION

#### Total Sulfur in Oil

#### Method P-0-11

#### SCOPE:

This method determines total sulfur in oil using the Leco Model Sulfur Analyzer. The method determines total sulfur at concentrations greater than 0.05%.

#### PROCEDURE:

The procedure is identical to Method P-S-10, "Total Sulfur in Shales," (For details of the procedure or calculations, refer to that method).

#### EQUIPMENT:

1. Gas Chromatograph, Hewlett-Packard 5712A. Any GC with a sample loop system, temperature-programmed oven, sub-ambient cooling, and TC detector, can be used.
2. Strip Chart Recorder, HP 7123A, or equivalent.
3. Integrator, S-P 1171A.
4. Drying tube, Supelco No. 020619.
5. Column, Supelco 1/8" x 30' ss, 50-80 x Porapak Q.
6. Bubble Flow Meter

#### REAGENTS:

1. Standard Gas Mixes, calibrated, (for analyses, see Table 2-1).
2. Carrier Gas, GC mixture, 9.5% hydrogen - 90.5% helium.



PAVING OIL SHALES DEMONSTRATION

Total Sulfur in Oil

Method P-2-11

SCOPE:

This method determines total sulfur in oil using the Leco Model Sulfur Analyzer. The method determines total sulfur at concentrations greater than 0.05%.

PROCEDURE:

The procedure is identical to Method P-2-10, "Total Sulfur in Shales," (for details of the procedure or calculations, refer to that method).

# PARAHO OIL SHALE DEMONSTRATION

## Gas Chromatographic Analysis of Product Gas

### Method P-G-01

#### SCOPE:

This method measures the component gases in the product gas recycle stream sample prepared by Method P-P-05. Calibration standards containing hydrogen, nitrogen, oxygen, carbon monoxide, methane, carbon dioxide, ethylene, ethane, propylene, propane, i-butane, n-butane, n-pentane, and n-hexane permit the quantitative measurement of these components. Other gases which can be detected by the GC system include: Nitrous oxide, nitric oxide, water, hydrogen sulfide, carbonyl sulfide, and argon. Detection limits are about 0.05 vol%.

#### OUTLINE:

A sample is transferred to a 0.5 cc sample loop where it is swept into the column with a hydrogen-helium (8.5% H<sub>2</sub>) carrier gas flowing at 30 cc/min. This column, 1/8" x 30' Porapak Q, is temperature-programmed at 32°C/min from -30°C to 200°C with 8 minute hold at the lower temperature and 32 minutes at the upper. Components are detected in a dual-column thermal conductivity detector. They are identified and measured on the basis of their retention times and response factors. About an hour is required for a complete analysis.

#### EQUIPMENT:

1. Gas Chromatograph, Hewlett-Packard 5712A. Any GC with a sample loop system, temperature-programmed oven, sub-ambient cooling, and TC detector, can be used.
2. Strip Chart Recorder. HP 7123A, or equivalent.
3. Integrator, H-P 3373B.
4. Drying tube, Supelco No. 020619.
5. Column, Supelco 1/8" x 30' ss, 50-80 m Porapak Q.
6. Bubble Flow Meter

#### REAGENTS:

1. Standard Gas Mixes, calibrated, (for analyses, see Table 2-1).
2. Carrier Gas, EC mixture, 8.5% hydrogen - 91.5% helium.



# PARAMO OIL SHALE DEMONSTRATION

## Gas Chromatographic Analysis of Product Gas

### Method 1-C-01

#### SCOPE:

This method measures the component gases in the product gas recycle stream sample prepared by Method 1-B-02. Calibration standards containing hydrogen, nitrogen, oxygen, carbon monoxide, methane, carbon dioxide, ethylene, ethane, propylene, propane, 1-butane, n-butane, n-pentane, and n-hexane permit the quantitative measurement of these components. Other gases which can be detected by the GC system include: Nitrous oxide, nitric oxide, water, hydrogen sulfide, carbonyl sulfide, and argon. Detection limits are about 0.02 vol%.

#### OUTLINE:

A sample is transferred to a 0.5 cc sample loop where it is swept into the column with a hydrogen-helium (8.5:1.5) carrier gas flowing at 30 cc/min. The column, 1/8" x 30' Porapak Q, is temperature-programmed at 120°C/min from -30°C to 200°C with 8 minute hold at the lower temperature and 32 minutes at the upper. Components are detected in a dual-column thermal conductivity detector. They are identified and measured on the basis of their retention times and response factors. About an hour is required for a complete analysis.

#### EQUIPMENT:

1. Gas Chromatograph, Hewlett-Packard 5713A. Any GC with a sample loop system, temperature-programmed oven, and ambient cooling, and TC detector, can be used.

2. Strip Chart Recorder, HP 7133A, or equivalent.

3. Integrator, M-7 3371B.

4. Drying tube, Supelco No. 020019.

5. Column, Supelco 1/8" x 30' ss, 50-80 m Porapak Q.

6. Bubble Flow Meter

#### REAGENTS:

1. Standard Gas Mixer, calibrated, (for analyses, see Table 1-1).

2. Carrier Gas, GC mixture, 8.5:1 hydrogen - 51.5:1 helium.

3. Carbon Dioxide, commercial cylinder fitted with eductor tube.
4. Air, 40 psig

PROCEDURE:

1. Prepare the chromatograph for routine operation.
  - a. If the instrument was shut off completely, refer to "Cold Start-up," Appendix 2-1.
  - b. If the instrument was shutdown overnight, refer to "Daily Start-up," Appendix 2-2.
2. Purge the appropriate sample or standard at the rate of 5-10 bubbles/min after the OVEN is turned "on." Purging should be continued for about 5 min.
3. Start the analysis when the OVEN Ready-Lite remains lit.
  - a. Stop purging.
  - b. Start program (in this sequence and without delay):
    - i. Turn sample loop to new position.
    - ii. Depress OVEN "start" button.
    - iii. Depress INTEGRATOR "start analysis" button.
4. After hydrogen is eluted (first peak appears and integration is completed,) flip polarity from A to B.
5. After the chromatogram is completed, flip polarity from B to A.
6. After all chromatograms are completed, shut down the GC. Follow "Daily Shutdown," Appendix 2-3, or "Long Term Shutdown," Appendix 2-4 depending upon the anticipated shutdown period.

CALULATIONS:

1. Retention time. Components are identified on the basis of their retention times (see Table 2-3).
  - a. Note any R.T. differing by more than 0.2 minutes from current mean value.
    - i. If more than 2 R.T.'s differ significantly, check the flow rates.
    - ii. If many R.T.'s differ significantly, the sample should be reanalyzed after the flow rates have been checked.
  - b. Note any extraneous peaks (R.T., and area) in the work book (P-L-6) and report sheet (P-L-7).



1. Carbon dioxide, compressed cylinder fitted with reductor tube.

4. Air, 40 psig

# PROCEDURE:

1. Prepare the chromatograph for routine operation.

a. If the instrument was shut off completely, refer to "Cold Start-up," Appendix 2-1.

b. If the instrument was shutdown overnight, refer to "Daily Start-up," Appendix 2-2.

2. Purge the chromatograph sample or standard at the rate of 5-10 ml/min after the OVEN is turned "on." Purging should be continued for about 5 min.

3. Start the analysis when the OVEN Ready-Lite remains lit.

a. Stop purging.

b. Start program (in this sequence and without delay):

i. Turn sample loop to new position.

ii. Depress OVEN "start" button.

iii. Depress INTEGRATOR "start analysis" button.

4. After hydrogen is started (first peak appears and integration is completed), flip polarity from A to B.

5. After the chromatogram is completed, flip polarity from B to A.

6. After all chromatograms are completed, shut down the GC. Follow "Daily Shutdown," Appendix 2-3, or "Long Term Shutdown," Appendix 2-4 depending upon the anticipated shutdown period.

# CALCULATIONS:

1. Retention time. Components are identified on the basis of their retention times (see Table 2-1).

a. Note any R.T. differing by more than 0.2 minutes from current mean value.

i. If more than 2 R.T.'s differ significantly, check the flow rates.

ii. If many R.T.'s differ significantly, the sample should be reanalyzed after the flow rates have been checked.

b. Note any extraneous peaks (R.T. and area) in the work book (2-5) and report sheet (2-6).

2. Response factors. Response factors are calculated about once a month using Standard Mixes 1, 3, 4 and air.

a. R.F. (all components except hydrogen)  $RF = P/A$   
where, P = known volume% (see Table 2-1 and  
A = area (expressed in mv-min)

b. R.F. (hydrogen)

$P = xA^3 + yA^2 + zA + k$  where x, y, z, and k are constants determined by a data fit using a computer. The usual hydrogen equation is:

$$P = 1.75A^3 - 10.23A^2 + 34.35A - 0.92$$

3. Determination of volume%

a. Individual, uncorrected.

$Vol\% = R.F. \times \text{area}$  (use formula 2b for hydrogen).

Enter all data in workbook (P-L-6).

b. Total, uncorrected

$\text{Total Vol}\% = \sum \text{Individual Vol}\%$

i. If Total Volume% is less than 95% or greater than 105%, check calculations for errors. If no errors are found, note, and rerun sample.

ii. Report Total Volume % on report sheet (P-L-7).

4. Normalization and dry basis

a. Factor =  $100\% / (\text{Total Volume \%} - \text{Vol\% Water})$ .

b. Normalized, dry basis = Factor x Vol% (step 3)

i. Do not calculate Vol% D.B. for water

ii. For hydrocarbons above propane, combine Vol% DB for C-4's, C-5's, and C-6's

iii. Report Vol%'s D.B. on report sheet (P-L-7)



2. Response factors. Response factors are calculated about once a month using Standard Mixes I, 2, 4 and air.

a. R.F. (all components except hydrogen)  $RF = P/A$  where, P = known values (see Table 1 and A = area (expressed in mv-min)

b. R.F. (hydrogen)

$P = kA^2 + yA^2 + zA + k$  where x, y, z, and k are constants determined by a data fit using a computer. The usual hydrogen equation is:

$$P = 1.75A^2 - 10.71A + 14.35A - 0.92$$

### 3. Determination of volumes

a. Individual, uncorrected.  
 $Vol = R.F. \times area$  (use formula 2b for hydrogen).  
 Enter all data in workbook (B-1-5).

b. Total, uncorrected  
 $Total\ Vol = \sum Individual\ Vol$   
 i. If Total Volume is less than 95% or greater than 105%, check calculations for errors. If no errors are found, note, and rerun sample.  
 ii. Report Total Volume / on report sheet (E-1-7).

### 4. Normalization and dry basis

a. Factor =  $100\% / (Total\ Volume - Vol\ Water)$   
 b. Normalized, Dry basis = Factor x Vol (step 3)  
 i. Do not calculate Vol's D.B. for water  
 ii. For hydrocarbons above propane, combine Vol's D.B. for C-4's, C-5's, and C-6's  
 iii. Report Vol's D.B. on report sheet (F-1-7)

TABLE 2-1

Standard GC Mixes - Method P-G-01

	<u>#1</u>	<u>#2</u>	<u>#3</u>	<u>#4</u>	<u>Air</u>
Hydrogen	4.8	15.1	29.7	50.0	
Nitrogen	60.6	26.0	1.4		78.1
Oxygen	0.45	0.29	0.12		21.0
Argon					0.93
Carbon Monoxide	3.8	7.8	13.2		
Methane	2.8	7.0	4.9	20.0	
Carbon Dioxide	25.1	33.9	44.9		
Ethylene	1.5	4.3	3.1	8.0	
Ethane	1.0	3.0	1.7	8.0	
Propylene				3.0	
Propane		2.7	0.99	3.0	
i-Butane				2.0	
n-Butane				2.0	
n-Pentane				2.0	
n-Hexane				2.0	



TABLE 2-1  
Standard GC Mixer - Method P-2-01

	#1	#2	#3	#4	Air
Hydrogen	4.8	10.1	20.7	20.0	
Nitrogen	60.0	20.0	1.4		78.1
Oxygen	0.42	0.29	0.12		21.0
Argon					0.93
Carbon Monoxide	3.8	7.8	13.2		
Methane	3.8	7.0	1.0	20.0	
Carbon Dioxide	25.1	23.9	44.9		
Ethylene	1.8	4.3	3.1	8.0	
Ethane	1.0	3.0	1.7	8.0	
Propylene				3.0	
Propane		2.7	0.99	3.0	
1-Butane				3.0	
n-Butane				3.0	
n-Pentane				3.0	
n-Hexane				3.0	

TABLE 2-2

Instrumental Settings - GC Analysis

5708A Control

Detector Temp.	200
Auxiliary Temp.	100
Inj. Port Temp.	Off

5705A TC Detector Control

Sensitivity	4
Offset	None
Polarity	B (A for H only)
Attenuation	$\infty$

5702A Oven Temp. Programmer

Time 1	8 min
Temp. 1	-30°C
Rate	32°C/min
Temp 2	200°C
Time 2	32 min
Oven Mode	Operate

3373B Integrator

Attenuation	1
Following buttons are depressed before starting an analysis:	
Stop Analysis	
Automatic Operation	Sensitivity 3

7123A Recorder

Detector	2
Pen	Down
Chart	Lo
Line	On



Table 2-2

Instrumental Settings - GC Analysis

5708A Control

Detector Temp. 300  
Auxiliary Temp. 100  
Inj. Port Temp. 055

5705A TC Detector Control

Sensitivity 4  
Offset None  
Polarity S (A for H only)  
Attenuation 00

5702A Oven Temp. Program

Time 1 8 min  
Temp. 1 -100°C  
Rate 32°C/min  
Temp. 2 100°C  
Time 2 32 min  
Oven Mode Operate

3375B Integrator

Attenuation 1  
Following buttons are depressed before starting an analysis:  
Stop Analysis  
Automatic Operation Sensitivity 3

7122A Recorder

Detector 2  
Pen Down  
Chart Lo  
Line On

TABLE 2-3

Retention Times

<u>Components</u>	<u>R.T. (min)</u>
Hydrogen	2.8
Nitrogen	4.7
Oxygen	5.5
Argon	5.8
Carbon Monoxide	6.1
Methane	11.8
Carbon Dioxide	14.7
Ethylene	16.3
Ethane	16.9
Water	17.9
Hydrogen Sulfide	18.0
Propylene	19.9
Propane	20.3
n-Butylene	24.8
n-Butane	25.5
n-Pentane	35.0
n-Hexane	53.4



TABLE 2-3

Retention Times

Components	R.T. (min)
Hydrogen	3.8
Nitrogen	4.7
Oxygen	5.2
Argon	5.8
Carbon Monoxide	6.1
Methane	11.8
Carbon Dioxide	14.7
Ethylene	16.3
Ethane	16.9
Water	17.9
Hydrogen Sulfide	18.0
Propylene	19.9
Propane	20.3
n-Butylene	24.8
n-Butane	25.9
n-Pentane	32.0
n-Hexane	33.4

SCOPE:

APPENDIX 2-1

"Cold" Startup - GC Analysis

SCOPE:

This procedure details the steps needed for a "cold" start-up (from a long term shutdown).

PROCEDURE:

1. Turn on carrier gas; (valve (6), Figure 2-4) check for leaks.
2. Increase pressure to 60 psig (valve (6), Figure 2-4).
3. Turn GC Line "on", and Detector Temperature to 200°C, and Auxiliary Temperature to 100°C.
4. Allow four hours for the detector temperature to equilibrate before starting with the Daily Start-up (Appendix 2-2).



APPENDIX 3-1  
"Cold" Startup - GC Analysis

SCOPE:

This procedure details the steps needed for a "cold" start-up (from a long term shutdown).

PROCEDURE:

1. Turn on carrier gas; (valve (6), Figure 3-4) check for leaks.
2. Increase pressure to 60 psig (valve (6), Figure 3-4).
3. Turn GC line "on", and Detector Temperature to 300°C, and Auxiliary Temperature to 100°C.
4. Allow four hours for the detector temperature to equilibrate before starting with the Daily Start-up (Appendix 3-2).

## APPENDIX 2-2

### Daily Start-up - GC Analysis

#### SCOPE:

This procedure details the steps needed for the routine daily start-up. This procedure follows the usual daily shutdown (Appendix 2-3) or the "cold" start-up (Appendix 2-1 ).

#### PROCEDURE:

1. Turn the TC Detector Control Sensitivity to "4" and oven mode to "operate."
2. Open air (valve (9) Figure 2-4).
3. Using the bubble flow meter adjust the carrier flows:  
A =  $20.5 \pm 0.2$  sec/10 cc; B =  $20.4 \pm 0.2$  sec/10 cc.
4. Adjust zero using Coarse Zero, Fine Zero, and Recorder Zero such that little or no pen movement occurs when the polarity is switched from A to B. Leave polarity on A.
5. Lower pen and turn Recorder Chart to "10."
6. Make sure that all switches on the GC are in the positions indicated in Table 2-2 before introducing any sample or standard to the chromatograph.



APPENDIX 3-2  
Daily Start-up - GC Analysis

SCOPE:

This procedure details the steps needed for the routine daily start-up. This procedure follows the usual daily shutdown (Appendix 3-3) or the "cold" start-up (Appendix 3-1).

PROCEDURE:

1. Turn the GC Detector Control Sensitivity to "4" and open mode to "operate".
2. Open air (valve (9) Figure 3-4).
3. Using the bubble flow meter adjust the carrier flow:  
 $A = 20.2 \pm 0.2 \text{ sec/10 cc}$ ;  $B = 20.4 \pm 0.2 \text{ sec/10 cc}$ .
4. Adjust zero using Coarse Zero, Fine Zero, and Recorder Zero such that little or no pen movement occurs when the polarity is switched from A to B. Leave polarity on A.
5. Lower pen and turn Recorder Chart to "10".
6. Make sure that all switches on the GC are in the positions indicated in Table 3-2 before introducing any sample or standard to the chromatograph.

## APPENDIX 2-3

## Daily Shutdown - GC Analysis

SCOPE:

This procedure details the shutdown steps needed for a short period (overnight or weekend). This procedure is not needed for shorter periods (portions of work day).

PROCEDURE:

1. Raise pen; turn "off", Oven Mode and Recorder Chart.
2. Close the air and carbon dioxide valves (valves (9) and (10), Figure 2-4).
3. Check all cylinders not in use (all except carrier gas) to be sure that no pressures are left in gauges. Open all diaphragm valves; close all other valves.
4. Check GC; only the GC Line and Detector Temperature Control lites should be lit. Recorder and Integrator line are "on" and lit.



# APPENDIX 2-3

## Daily Shutdown - GC Analysis

### SCOPE:

This procedure details the shutdown steps needed for a short period (overnight or weekend). This procedure is not needed for shorter periods (portions of work day).

### PROCEDURE:

1. Raise pen: turn "off", Oven Mode and Recorder Chart.
2. Close the air and carbon dioxide valves (valves (3) and (10), Figure 2-4).
3. Check all cylinders not in use (all except carrier gas) to be sure that no pressures are left in gauges. Open all diaphragm valves; close all other valves.
4. Check GC; only the GC line and detector temperature control lines should be left. Recorder and Integrator line are "on" and left.

## APPENDIX 2-4

## Long Term Shutdown - GC Analysis

SCOPE:

This procedure details the steps needed whenever a long term shutdown (more than three days) is anticipated. The procedure is also used whenever the carrier gas flow is interrupted; i.e. changing carrier gas cylinders, drying tubes, septums, columns.

PROCEDURE:

1. After Step 3, Daily Shutdown (Appendix 2-3), turn "off" Detector Temperature Control and GC, Integrator, and Recorder Line.
2. Turn "off" the carrier gas flow (valve (6), Figure 2-4).
3. Be certain that no pressures are left in any cylinder gauges. Open all diaphragm valves; close all other valves.
4. No lites should be lit on the GC instrument; all power is off; no gas is flowing.



APPENDIX 3-4

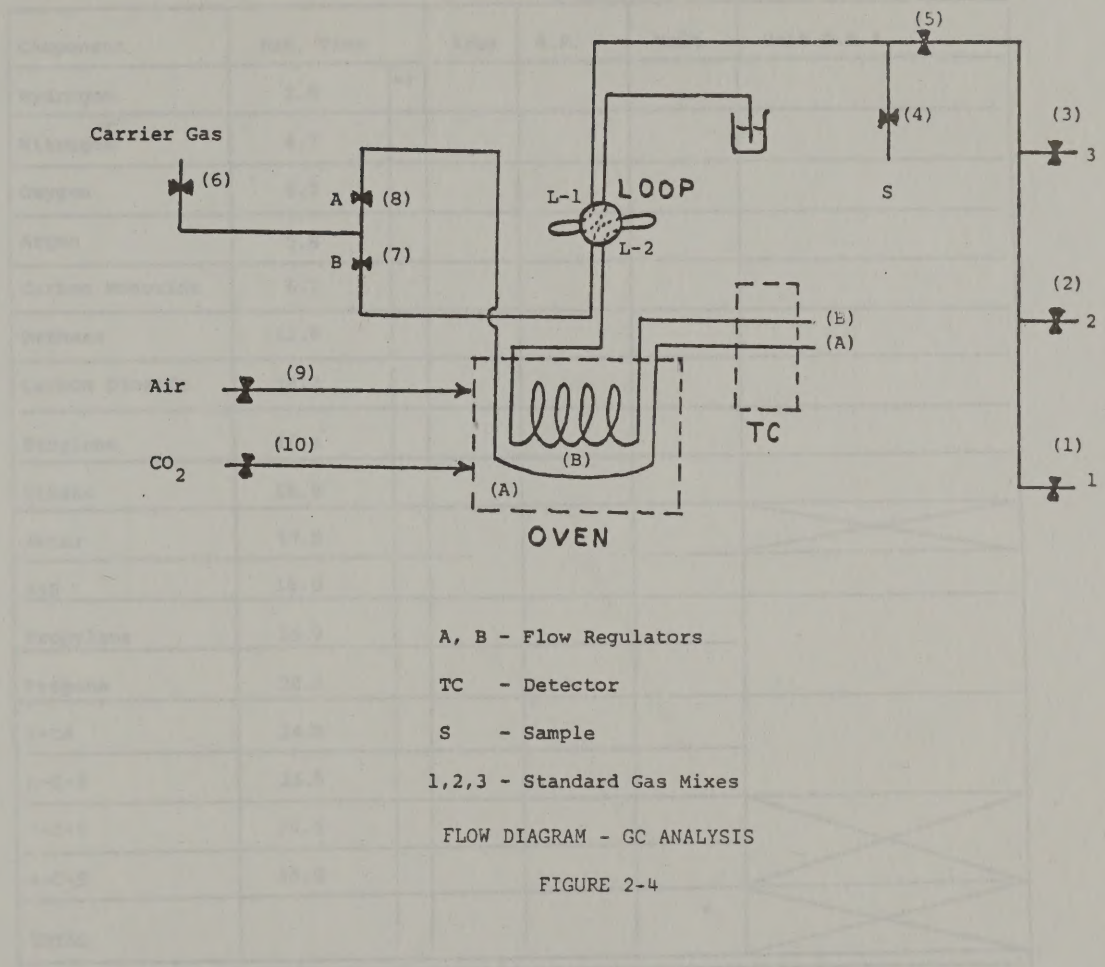
Long Term Shutdown - GC Analysis

NOTE:

This procedure details the steps needed whenever a long term shutdown (more than three days) is anticipated. The procedure is also used whenever the carrier gas flow is interrupted; i.e., changing carrier gas cylinders, drying tubes, septums, columns.

PROCEDURE:

1. After Step 3, Daily Shutdown (Appendix 3-3), turn "off" Detector Temperature Control and GC, Integrator, and Recorder lines.
2. Turn "off" the carrier gas flow (valve (C), Figure 3-4).
3. Be certain that no pressures are left in any cylinder gauges. Open all discharge valves; close all other valves.
4. No lines should be left on the GC instrument; all power is off; no gas is flowing.





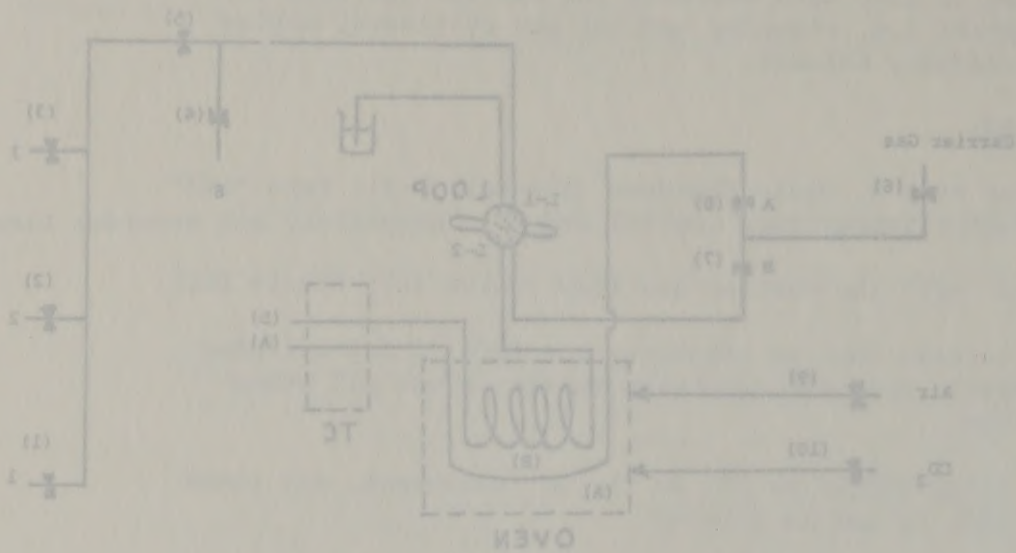
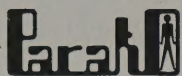


FIGURE 1-4  
 FLOW DIAGRAM - GC ANALYSIS  
 1, 2, 3 - Standard Gas Mixers  
 S - Sample  
 TC - Detector  
 A, B - Flow Regulators



## PARAHO PROJECT

## GAS CHROMATOGRAPHY SAMPLE

Sample Description\* \_\_\_\_\_

Run No.\* \_\_\_\_\_ Date\* \_\_\_\_\_

Sample No.\* \_\_\_\_\_ Time\* \_\_\_\_\_

Component	Ret. Time	Area	R.F.	Vol%	Vol% D.B.*
Hydrogen	2.8	**			
Nitrogen	4.7				
Oxygen	5.5				
Argon	5.8				
Carbon Monoxide	6.1				
Methane	11.8				
Carbon Dioxide	14.7				
Ethylene	16.3				
Ethane	16.9				
Water	17.9				
H <sub>2</sub> S	18.0				
Propylene	19.9				
Propane	20.3				
i-C <sub>4</sub>	24.9				
n-C-4	25.5				
i-C-5	34.5				
n-C-5	35.0				
TOTAL				*	

\*Report data on P-L-7

\*\*If R.T. does not agree within  $\pm 0.2$  min of mean, place an "X" in this column.

$$\text{Factor} = \frac{100\%}{\text{Total Vol\%} - \text{Vol\% Water}} = \frac{100\%}{\text{---} - \text{---}} = \text{---}$$

COMMENTS:

Analyst \_\_\_\_\_

Date \_\_\_\_\_

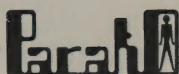


11-11-3

WESTON BOND

ELIOT

22 COTTON FIBRE



## PARAHO OIL SHALE DEMONSTRATION

### Recycle Condensate (Ambient)

#### Method P-G-02

#### SCOPE:

The method measures and characterizes the material condensed from recycle gas at 70°F. All concentrations are calculated on the wet recycle gas as it exists in the retort system.

#### OUTLINE:

The condensate is separated into the water and oil (heavy naphtha) portions. Both portions are measured. Gravity (°API) is determined on the oil. Volume percents of both are calculated from the measured quantities of water, oil, and dry gas.

#### PROCEDURE:

1. Transfer entire condensate to a 1000 ml separatory funnel. Weigh empty sample bottle to nearest 0.1 gm (W-1).
2. Drain water layer into sample bottle and reweigh to nearest 0.1 gm (W-2).
3. Drain oil layer into suitable graduated cylinder tared to nearest 0.1 gm (W-3).
4. Record oil volume to nearest ml (nearest 0.5 ml if less than 25 ml total) and reweigh to nearest 0.1 gm (W-4).
5. Record volume of uncorrected dry gas from wet test meter.

#### CALCULATIONS:

1. Wt. Water (gm) = W-2 - W-1
2. Wt. Hv.Nap. (gm) = W-4 - W-3
3. Volume, SCF, dry gas = (WTM x 0.8) + 1.0\*
4. Volume, SCF, water = gm. H<sub>2</sub>O x 0.0465
5. Volume, SCF, Hv. Nap. = gm. Hv. Nap. x 0.837/MW (1)
6. Volume, SCF, total = volume, dry gas + water + hv. naph.

(1) Refer to attached table to obtain MW from °API.

\*Add 1.0 to value only if sample goes through on stream G.C.



WATER-OIL SHALE DEMONSTRATION

Recycle Condensate (Asphalt)

Method 1-4-02

NOTE:

The entire material and condensate is recycled. The material condensed from recycle gas at 10% A/I concentrations are collected as the wet recycle gas as it exists in the reactor system.

QUALITY:

The condensate is separated into the water and oil (heavy naphthalene) portions. Both portions are measured. Gravity (SG) is determined on the oil. Volume percent of both are obtained from the measured quantities of water, oil, and dry gas.

PROCEDURE:

1. Transfer entire condensate to a 1000 ml separator funnel. Weigh empty sample bottle to nearest 0.1 gm (W-1).
2. Drain water layer into sample bottle and weigh to nearest 0.1 gm (W-2).
3. Drain oil layer into suitable graduated cylinder rated to nearest 0.1 gm (W-3).
4. Remove oil volume to nearest ml (nearest 0.5 ml if less than 25 ml total) and weigh to nearest 0.1 gm (W-4).
5. Record volume of uncorrected dry gas from wet test meter.

CALCULATIONS:

1. Wt. Water (gm) = W-2 - W-1
2. Wt. Bitumen (gm) = W-4 - W-3
3. Volume, SCF, dry gas =  $(W-4 - W-3) \times 0.85 + 1.0$
4. Volume, SCF, water =  $gm \cdot H_2O \times 0.0455$
5. Volume, SCF, dry gas =  $gm \cdot H_2O \times 0.85 + 1.0$
6. Volume, SCF, total = volume, dry gas + water + dry gas.

(1) Refer to attached table to obtain Wt. % gas.  
\*Add 1.0 to value only if sample was through an screen 20.

$$\text{*Volume \% Water} = (\text{Water SCF}/\text{total SCF}) \times 100\%$$

$$\text{*Volume \% Hv. Naphtha} = (\text{Lt. Nap SCF}/\text{total SCF}) \times 100\%$$

$$\text{*Hv. Naphtha, Gal/MSCF} = (\text{ml hv. nap.}/\text{total SCF}) \times 0.264$$

$$\text{*Hv. Naphtha } ^\circ\text{API} = [(141.5 \times \text{ml hv. nap})/\text{gm hv. nap}] - 132.2$$

Data marked with an asterisk (\*) are reported. Volume % Water and  $^\circ\text{API}$  are reported to 3 significant figures; Volume % and Gal/MSCF heavy naphtha, to 2 significant figures.

43	152
44	153
45	154
46	155
47	156
48	157
49	158
50	159
51	160
52	161
53	162
54	163
55	164
56	165
57	166
58	167
59	168
60	169

NOTE: The above table was obtained from the equation:

$$\text{API} = 504.7 - 13.7 (\text{API}) + 0.001 (\text{API})^2$$

The equation was generated from data from Table 1, Series 2-20-76 and Group IV, page 21 from Hummel's Data Book.



\*Volume of Water = (Water SCT/total SCT) x 100%

\*Volume of H<sub>2</sub>O Nephthys = (H<sub>2</sub>O Neph SCT/total SCT) x 100%

\*H<sub>2</sub>O Nephthys, Cal/MCT = (H<sub>2</sub>O Neph. SCT/total SCT) x 0.264

\*H<sub>2</sub>O Nephthys <sup>2</sup>API = [(191.5 x H<sub>2</sub>O Neph. SCT/total SCT) - 132.2]

Data marked with an asterisk (\*) are reported. Volume of Water and <sup>2</sup>API are reported to 3 significant figures; Volume of H<sub>2</sub>O Nephthys, Cal/MCT heavy nephthys, to 2 significant figures.

# Resin Condensate (Sub-ambient)

$^{\circ}\text{API}$  - MW (Molecular Wt)

$^{\circ}\text{API}$	MW
35	188
36	182
37	177
38	172
39	167
40	162
41	157
42	152
43	148
44	143
45	139
46	135
47	132
48	128
49	125
50	122
51	119
52	116
53	113
54	111
55	109
56	107
57	105
58	103
59	102
60	100

NOTE: The above table was obtained from the equation:

$$\text{MW} = 504.7 - 12.3 (^{\circ}\text{API}) + 0.92 (^{\circ}\text{API})^2$$

The equation was generated from data from Table I, Memo. 2-20-76 and Group IV, page 23 from Maxwell's Data Book.



100

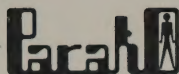
APL - MW (Molecular Wt)

APL	MW
100	100
101	101
102	102
103	103
104	104
105	105
106	106
107	107
108	108
109	109
110	110
111	111
112	112
113	113
114	114
115	115
116	116
117	117
118	118
119	119
120	120
121	121
122	122
123	123
124	124
125	125
126	126
127	127
128	128
129	129
130	130
131	131
132	132
133	133
134	134
135	135
136	136
137	137
138	138
139	139
140	140
141	141
142	142
143	143
144	144
145	145
146	146
147	147
148	148
149	149
150	150

NOTE: The above table was obtained from the equation:

$$MW = 204.7 - 12.1 (\text{APL}) + 0.92 (\text{APL})^2$$

The equation was generated from data from Table 1, Rows 1-20-75 and Group IV, page 13 from Maxwell's Data Book.



## PARAHO OIL SHALE DEMONSTRATION

### Recycle Condensate (Sub-Ambient)

#### Method P-G-03

##### SCOPE:

The method measures and characterizes the material condensed from "dry" recycle gas at sub-ambient conditions using a dry ice-acetone bath. "Dry" recycle gas is gas that has passed through the water-jacketed condenser used to obtain the ambient recycle condensate, Method P-G-02.

##### OUTLINE:

The condensate is separated into water and light naphtha portions. Both portions are measured. The wet test meter reading for dry gas is corrected to SCF and the gravity ( $^{\circ}\text{API}$ ) of the light naphtha is calculated. The weights of water (gm) and light naphtha (gm), the volumes of dry gas (SCF) and light naphtha (ml), and the gravity ( $^{\circ}\text{API}$ ) of the light naphtha are reported.

##### EQUIPMENT:

1. Gas washing bottles, 250 ml. with plain tip (no sintered glass diffusers).

##### PROCEDURE:

1. Two gas washing bottles are arranged, in series, between the laboratory GC sample bomb and the wet test meter. The bottles are immersed about 2/3 in a dry ice-acetone bath.
2. Gas is passed through the system at about 15 CF/hrs until 10-20 CF is registered on the wet test meter.
3. The laboratory procedure is the same as steps 1-5 PROCEDURE, Method P-G-02.

##### CALCULATIONS:

1.  $\text{Wt Water (gm)} = \text{W-2} - \text{W-1}$
2.  $\text{Wt Lt. Naph. (gm)} = \text{W-4} - \text{W-2}$
3.  $\text{Vol, Lt. Naph. (ml)}$
4.  $\text{Vol, SCF, dry gas,} = (\text{WTM} \times 0.8)$
5.  $\text{Lt. Naphtha, } ^{\circ}\text{API} = \left[ (141.5 \times \text{ml. lt. naph}) / \text{gm. lt. naph.} \right] - 132.2$

All data are reported: Wts, Water and Lt. Naph., and  $^{\circ}\text{API}$  to nearest 0.1; Volume, Dry Gas to nearest 0.01 SCF; and Volume, Lt. Naph. to nearest ml.



SCOPE:

The method measures and characterizes the material condensed from "dry" residue gas at sub-ambient conditions using a dry ice-acetone bath. "Dry" residue gas is gas that has passed through the water-jacketed condenser used to obtain the ambient residue condensate. Method P-5-03.

OUTLINE:

The condensate is separated into water and light naphtha portions. Both portions are measured. The wet test meter reading for dry gas is corrected to SCT and the gravity (GAP) of the light naphtha is calculated. The weights of water (gm) and light naphtha (gm), the volume of dry gas (SCT) and light naphtha (ml), and the gravity (GAP) of the light naphtha are reported.

EQUIPMENT:

1. Gas washing bottles, 250 ml. with plain tip (no sintered glass diffusion).

PROCEDURE:

1. Two gas washing bottles are arranged, in series, between the laboratory GC sample head and the wet test meter. The bottles are immersed about 2/3 in a dry ice-acetone bath.
2. Gas is passed through the system at about 15 CFHrs until 10-20 CF is registered on the wet test meter.
3. The laboratory procedure in the same as steps 1-5 PROCEDURE, Method P-5-03.

CALCULATIONS:

1. Wt Water (gm) = W-1
2. Wt Lt. Naph. (gm) = W-4 - W-3
3. Vol. Lt. Naph. (ml)
4. Vol. SCT, dry gas = (W-1 x 0.8)
5. Lt. Naphtha, GAP =  $\left[ \frac{141.5 \times \text{ml. Lt. Naph.}}{\text{Wt. Lt. Naph.}} \right] - 132.5$

All data are reported: Wt. Water and Lt. Naph., and Vol. to nearest 0.1 Volume, Dry Gas to nearest 0.01 SCT, and Volume, Lt. Naph. to nearest ml.

# PARAHO OIL SHALE DEMONSTRATION

## Recycle Gas Contaminants

### Method P-G-04

#### SCOPE:

Methods are detailed for the determination of ammonia, hydrogen sulfide, sulfur dioxide, and oxides of nitrogen in recycle gas or effluents from the thermal oxidizer or heater stacks. Because of high water vapor concentrations and solubilities of ammonia and hydrogen sulfide, absorbers are used to sample recycle gas for these contaminants. Grab samples using glass bombs are used for the other tests.

#### A. Ammonia

#### OUTLINE:

Ammonia is absorbed in dilute acid solution. After adding excess caustic, the ammonia is steam distilled into a boric acid solution and titrated with standard acid. Other basic gases, if present, would interfere.

#### APPARATUS:

1. Gas absorber, 500 ml, fitted with a sintered glass disc or glass sampling bomb, 500 ml.
2. Distillation apparatus, water-jacketed condenser.
3. Titrimeter

#### REAGENTS:

1. Absorber solution, 1% sulfuric acid.
2. Borte buffer. Dissolve 2.5 gm sodium borate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) and 2.5 gm sodium hydroxide in 1 liter of distilled water.
3. Boric acid absorber, 2% boric acid
4. Titrant, 0.02 N  $\text{H}_2\text{SO}_4$

#### PROCEDURE:

1. Add about 100 ml of absorber solution to the absorber and pass 0.5 CF of gas. (Add 25 ml of absorber solution to grab sample in glass bomb).
2. Transfer the contents to the distillation flask. Rinse with distilled water and add rinsings to the flask. Dilute to about 200 ml with distilled water.



# Recovery Gas Concentration

Method 7-2-04

## SCOPE

Methods are detailed for the determination of ammonia, hydrogen sulfide, sulfur dioxide, and oxides of nitrogen in recovery gas or effluents from the thermal oxidizer or heater stacks. Because of high water vapor concentrations and solubilities of ammonia and hydrogen sulfide, absorbers are used to sample recovery gas for these constituents. Grab samples using glass bottles are used for the other gases.

## A. Ammonia

## OUTLINE

Ammonia is absorbed in dilute acid solution. After adding excess boric acid, the ammonia is steam distilled into a boric acid solution and titrated with standard acid. Other basic gases, if present, would interfere.

## APPARATUS

1. Gas absorber, 500 ml, fitted with a sintered glass disc or glass sampling head, 500 ml.

2. Distillation apparatus, water-jacketed condenser.

3. Titrimeter

## REAGENTS

1. Absorber solution, 1% sulfuric acid.

2. Boric buffer. Dissolve 2 g sodium borate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) and 2.5 g sodium hydroxide in 1 liter of distilled water.

3. Boric acid absorber, 1% boric acid

4. Titrant, 0.02 N  $\text{H}_2\text{SO}_4$

## PROCEDURE

1. Add about 100 ml of absorber solution to the absorber and pass 0.5 CF of gas. (Add 15 ml of absorber solution to grab sample in glass bottle).

2. Transfer the contents to the distillation flask. Rinse with distilled water and add rinsings to the flask. Dilute to about 100 ml with distilled water.

3. Add 25 ml of borate buffer to the flask and 50 ml of boric acid absorber to the receiver.
4. Distill over about 100 mls at a rate of 6-10 mls/min.
5. (For stack samples, proceed to step 7) Transfer the distillate to a 250 ml volumetric flask. Rinse the receiver with distilled water and add rinsings to the volumetric flask. Dilute to volume.
6. Place a suitable aliquot in a 150 ml beaker, and if necessary, dilute with distilled water.
7. Titrate with the acid titrant.

#### CALCULATIONS:

1. Recycle gas, vol%  $\text{NH}_3$ , dry basis:

$$\begin{aligned} \% \text{NH}_3 &= \frac{\text{ml. titr.} \times 0.02 \text{ mg-eq/ml} \times 379 \text{ SCF/lb-mol} \times 100\% \times 250}{1000 \text{ mg/gm} \times \text{eq/mol} \times 453.6 \text{ gm/lb} \times (0.5 \times 0.8) \text{ SCF} \times A} \\ &= 1.02 \times \frac{\text{ml titr}}{A}, \text{ where } A = \text{ml. Aliquot} \end{aligned}$$

2. Stack gas, vol%  $\text{NH}_3$ , wet basis:

$$\begin{aligned} \% \text{NH}_3 &= \frac{\text{ml titr.} \times 0.02 \text{ mg-eq/ml} \times 22.4 \text{ ml/mg-mol} \times 100\%}{\text{eq/mol} \times (500 \times 24/30 \times 273/294) \text{ ml STP}} \\ &= 0.121 \times \text{ml titr.} \end{aligned}$$

#### B. Hydrogen sulfide

#### OUTLINE:

Hydrogen sulfide is absorbed in caustic. The solution is titrated potentiometrically with standard silver nitrate.

#### APPARATUS:

1. Gas absorbers (see A. Ammonia)
2. Titrimeter

#### REAGENTS:

1. Absorber, 5% sodium hydroxide
2. Ammonium hydroxide
3. Titrant, 0.01 N  $\text{AgNO}_3$



3. Add 25 ml of barium hydroxide to the flask and 50 ml of barium acid absorbent to the receiver.
4. Distill over about 100 ml at a rate of 5-10 ml/min.
5. (For start sample, proceed to step 7) Transfer the distillate to a 150 ml volumetric flask. Rinse the receiver with distilled water and add rinsings to the volumetric flask. Dilute to volume.
6. Place a suitable aliquot in a 150 ml beaker, and if necessary, dilute with distilled water.
7. Titrate with the acid titrant.

CALCULATIONS:

$$1. \text{ Barium gas, vol. ml, dry basis:}$$

$$\text{ml titr.} \times 0.02 \text{ eq/ml} \times 179 \text{ g/mol} \times 1000 \times 1000$$

$$\text{mg} = \frac{1000 \text{ eq/mol} \times 0.02 \text{ eq/ml} \times 179 \text{ g/mol} \times (0.8 \times 0.8) \text{ g} \times A}{\text{ml titr.}}$$

$$A, \text{ where } A = \text{ml. Aliquot}$$

$$2. \text{ Stack gas, vol. ml, wet basis:}$$

$$\text{ml titr.} \times 0.02 \text{ eq/ml} \times 22.4 \text{ ml/mol} \times 1000$$

$$\text{mg} = \frac{\text{eq/mol} \times (100 \times 14/10 \times 22.4/22.4) \text{ ml}}{\text{ml titr.}}$$

$$= 0.131 \times \text{ml titr.}$$

3. Hydrogen sulfide

NOTES:

Hydrogen sulfide is absorbed in caustic. The solution is titrated potentiometrically with standard silver nitrate.

APPARATUS:

1. Gas absorber (see A. ammonia)
2. Titillator

REAGENTS:

1. Ammonia, 28 sodium hydroxide
2. Ammonium hydroxide
3. Titrant, 0.01 N silver

#### PROCEDURE:

1. Add about 100 ml of absorber solution to the absorber and pass 0.5 CF of gas. (Add 25 ml of absorber solution to grab sample in glass bomb).
2. Transfer contents to a 250 ml volumetric flask. Rinse with distilled water and add rinsings to the flask. Dilute to volume with distilled water.
3. Place a suitable aliquot in a 150 ml beaker; if necessary add distilled water.
4. Adjust solution to 5% sodium hydroxide, add 1 ml of ammonia.
5. Titrate with the silver nitrate titrant using 500 mv full scale.

#### CALCULATIONS:

1. Recycle gas, vol%  $H_2S$ , dry basis:

$$\%H_2S = \frac{\text{ml titr.} \times 0.01 \text{ mg-eq/ml} \times 379 \text{ SCF/lb-mol} \times 100\% \times 250}{1000 \text{ mg/gr} \times 2 \text{ eq/mol} \times 453.6 \text{ gm/lb} \times (0.5 \times 0.8) \text{ SCF} \times A}$$

$$= 0.261 \times \frac{\text{ml titr.}}{A}$$

2. Stack gas, vol%  $H_2S$ , wet basis

$$\%H_2S = \frac{\text{ml titr} \times 0.01 \text{ mg eq/ml} \times 22.4 \text{ li/gm-mol} \times 100\% \times 250}{2 \text{ eq/mol} \times (500 \times 24/30 \times 273/294) \text{ ml STP} \times A}$$

$$= 7.54 \times \frac{\text{ml titrant}}{A}$$

#### C. Sulfur Dioxide

#### OUTLINE:

Sulfur dioxide is determined on a 500 ml grab sample using the West-Gaeke procedure. A solution of sodium tetrachloromercurate absorbs and stabilizes the sulfur dioxide. A red-colored complex ( $\lambda_{\text{max}} = 560 \text{ nm}$ ) is formed by the addition para-rosaniline hydrochloride and formaldehyde.

#### EQUIPMENT:

1. Sampling bomb, glass 500 ml.
2. Colorimeter



# PROCEDURE:

1. Add about 100 ml of absorber solution to the absorber and pass 0.2 cu of gas. (Add 25 ml of absorber solution to grab sample in glass bomb).
2. Transfer contents to a 250 ml volumetric flask. Rinse with distilled water and add rinsings to the flask. Dilute to volume with distilled water.
3. Place a suitable aliquot in a 150 ml beaker; if necessary add distilled water.
4. Adjust solution to 5% sodium hydroxide, add 1 ml of ammonia.
5. Titrate with the silver nitrate titrant using 500 mv full scale.

# CALCULATIONS:

1. Recycle gas, vol % H<sub>2</sub>, dry basis:

$$H_2 = \frac{1000 \text{ mg/gr} \times 1 \text{ eq/mol} \times 427.6 \text{ g/lb} \times (0.2 \times 0.8) \text{ SCV} \times A}{\text{ml liter} \times 0.01 \text{ eq/ml} \times 379 \text{ SCV/lb-mol} \times 1000 \times 250} = 0.261 \times \frac{\text{ml liter}}{A}$$

2. Stack gas, vol % H<sub>2</sub>, wet basis:

$$H_2 = \frac{1 \text{ eq/mol} \times 1600 \times 24/30 \times 273/273 \text{ ml STP} \times A}{\text{ml liter} \times 0.01 \text{ eq/ml} \times 22.4 \text{ liter-mol} \times 1000 \times 250} = 7.24 \times \frac{\text{ml liter}}{A}$$

# C. Sulfur Dioxide

# OUTLINE:

Sulfur dioxide is determined on a 500 ml grab sample using the West-Gaeke procedure. A solution of sodium tetrachloroaurate absorbs and stabilizes the sulfur dioxide. A red-colored complex (λ<sub>max</sub> = 580 mμ) is formed by the addition para-rosaniline hydrochloride and formaldehyde.

# EQUIPMENT:

1. Sampled bomb, glass 500 ml
2. Colorimeter

#### REAGENTS:

1. Sodium tetrachloro-mercurate (TCM), 0.02 M mercuric chloride ( $HgCl_2$ ) and 0.4 M sodium chloride.
2. Paraosaniline hydrochloride (PRA) 50 ml 0.2% dye + 50 ml HCl (R.G.), dilute to 1 liter with distilled water.
3. Formaldehyde. Dilute 5 ml formaldehyde (R.G.) to 1 liter with distilled water.

#### PROCEDURE:

1. Obtain a grab sample in a 500 ml gas bomb.
2. Inject 20 ml of TCM into the bomb.
3. Drain into a 50 ml volumetric flask.
4. Rinse with 2 x 5 ml distilled water and place into volumetric flask.
5. Add 5 ml PRA and shake.
6. Add 5 ml formaldehyde and shake.
7. Dilute to volume with distilled water and shake.
8. After 15 minutes, read absorbance at 560 nm.

#### CALCULATIONS:

$SO_2$ , ppm (v:v), wet basis =  $102 \times (abs - 0.020)$

#### D. Nitrogen Oxides

#### OUTLINE:

Total oxides of nitrogen are determined on a 500 ml grab sample using the EPA-approved method of phenoldisulfonic acid method. The yellow-colored complex ( $\lambda_{max} = 420 \text{ nm}$ ) is measured as nitric oxide ( $NO_2$ ).

#### EQUIPMENT:

(same as method C. Sulfur Dioxide)

#### REAGENTS:

1. Absorber, 2.8 ml  $H_2SO_4$  (R.G.) diluted to 1 liter with distilled water. Add 6 ml 3%  $H_2O_2$ . Make fresh weekly.



REAGENTS:

1. Sodium arsenochloride (TCM), 0.02 N arsenic chloride (0.01 g/l and 0.4 M sodium chloride).
2. Potassium dihydrogen phosphate (KHA) 50 ml 0.2% dye + 50 ml HCl (R.G.) dilute to 1 liter with distilled water.
3. Formaldehyde. Dilute 5 ml formaldehyde (R.G.) to 1 liter with distilled water.

PROCEDURE:

1. Obtain a grab sample in a 500 ml gas bomb.
2. Inject 20 ml of TCM into the bomb.
3. Drain into a 50 ml volumetric flask.
4. Rinse with 1 x 5 ml distilled water and place into volumetric flask.
5. Add 5 ml KHA and shake.
6. Add 5 ml formaldehyde and shake.
7. Dilute to volume with distilled water and shake.
8. After 15 minutes, read absorbance at 580 mμ.

CALCULATIONS:

20% (w/v), wet basis x 100 x (abs - 0.020)  
D. Nitrogen Oxides

NOTES:

Total oxides of nitrogen are determined on a 500 ml grab sample using the EPA-approved method of phosphoric acid method. The yellow-colored complex ( $\lambda_{max} = 420 \text{ m}\mu$ ) is measured as nitric oxide ( $\text{NO}_2$ ).

REMARKS:

(same as method C. Sulfur Dioxide)

REAGENTS:

1. Absorbance, 2.8 ml  $\text{H}_2\text{SO}_4$  (R.G.) diluted to 1 liter with distilled water. Add 5 ml 1%  $\text{H}_2\text{O}_2$ . Make fresh weekly.

## PARATEK OIL SHALE DEMONSTRATION

2. Phenoldisulfonic Acid Solution (PDS).
3. Sodium Hydroxide, 4%.
4. Sulfuric Acid, (R.G.)
5. Ammonium Hydroxide, (R.G.)

### PROCEDURE:

1. Obtain a grab sample in a 500 ml gas bomb.
2. Inject 25 ml of absorber into bomb; shake and allow to sit for 16 hours.
3. Drain into a 250 ml beaker; wash with 2 x 10 ml portions of distilled water.
4. Neutralizedropwise (25-35 drops) with 4% NaOH.
5. Evaporate to dryness.
6. Add 2 ml of PDS and titurate thoroughly.
7. Add 1 ml of water and 4 drops of  $H_2SO_4$ . Warm for a few minutes.
8. Cool, neutralize with  $NH_4OH$ .
9. Transfer to a 100 ml volumetric flask and measure absorbance at 420 nm.

### CALCULATIONS:

$NO_x$ , ppm (v:v) wet basis =  $841 \times \text{abs}$



1. Phenolphthalein Acid Solution (POS).
2. Sodium Hydroxide, 4N.
3. Sulfuric Acid, (R.G.).
4. Ammonium Hydroxide, (R.G.).

PROCEDURE:

1. Obtain a grab sample in a 500 ml gas bomb.
2. Inject 25 ml of absorber into bomb; shake and allow to sit for 16 hours.
3. Drain into a 150 ml beaker; wash with 2 x 10 ml portions of distilled water.
4. Neutralize dropwise (15-25 drops) with 4N NaOH.
5. Evaporate to dryness.
6. Add 2 ml of POS and titrate thoroughly.
7. Add 1 ml of water and 4 drops of H<sub>2</sub>SO<sub>4</sub>. Warm for a few minutes.
8. Cool, neutralize with NH<sub>4</sub>OH.
9. Transfer to a 100 ml volumetric flask and measure absorbance at 410 mμ.

CALCULATIONS:

NO<sub>x</sub>, ppm (v/v) wet basis =  $\frac{A}{A_0} \times 100 \times \frac{1}{V} \times 10^6$

# PARAHO OIL SHALE DEMONSTRATION

## Mist Particle Size Characterization

### Method P-G-05

#### SCOPE:

This method determines the mist particle size and loading at various points in the product gas system. Sites samples include off gas collectors, between the coalescer and ESP, and blower suction.

#### OUTLINE:

The gas stream is sampled isothermally (well above the dew-point of water) for a fixed time through a Delron Cascade Jet Impactor. Conditions are designed to attain isokinetic sampling. The Jet Impactor consist of a series of decreasing orifices with a plate positioned at a critical distance below each orifice. Total material collected is a measure of the mist loading and the distribution of the material on the various plates is a measure of the mist particle size.

#### APPARATUS:

1. Cascade Jet Impactor, Delron Model DCI-6
2. Impactor Box.
3. Probes, tips, and extensions.
4. Vacuum pump.

#### PROCEDURE:

1. Select proper probe tip (see Appendix 2-5).
2. Obtain tare weights on all plates and filter paper to nearest 0.1 mg.
3. Assemble the Jet Impactor with the stages and plates in proper order (stage #1 on top to stage #6 on bottom).
4. Place the assembled Jet Impactor in a 220°F oven for an hour before taking a sample. During that period, preheat the impaction box to 200°F at the sampling site.
5. Using a special carrying case, take the preheated Jet Impactor to the sampling site and assemble the apparatus as shown in Figure 2-5.



# PARADOX OIL STATE DEMONSTRATION

## Mist Particle Size Characterization

Method P-0-02

### SCOPE

This method determines the mist particle size and loading at various points in the product gas system. Sites sampled include all gas collectors, between the collector and ESP, and blower suction.

### OUTLINE

The gas stream is sampled isothermally (well above the dew-point of water) for a fixed time through a Dairon Cascade Jet Impactor. Conditions are designed to attain isokinetic sampling. The Jet Impactor consists of a series of concentric cylinders with a plate positioned at a critical distance below each orifice. Total material collected is a measure of the mist loading and the distribution of the material on the various plates is a measure of the mist particle size.

### APPARATUS

1. Cascade Jet Impactor, Dairon Model DCI-2
2. Impactor Box
3. Probes, tips, and extensions
4. Vacuum pump

### PROCEDURE

1. Select proper probe tip (see Appendix 3-2).
2. Obtain tare weights on all plates and filter paper to nearest 0.1 mg.
3. Assemble the Jet Impactor with the screen and plates in proper order (stage 41 on top to stage 48 on bottom).
4. Place the assembled Jet Impactor in a 750°F oven for an hour before taking a sample. During that period, preheat the impaction box to 750°F at the sampling site.
5. Using a special carrying cart, take the preheated Jet Impactor to the sampling site and assemble the apparatus as shown in Figure 3-2.

2. Draw a straightline through the points.
6. Turn on the vacuum pump pulling sample through the bypass line.

7. Actuate the solenoid valves to obtain a sample for the proper time:

Off gas collectors	40 sec
Coalescer - ESP	1 min
Blower suction	45 min

8. Turn off pump and heater, disassemble apparatus and carefully return the Jet Impactor to the laboratory.

9. Disassemble the Jet Impactor and reweigh the plates and filter paper.

10. Wipe out the cones with a tared tissue and reweigh to obtain the sample that did not adhere to plates or filter.

#### CALCULATIONS:

First, set up this table:

Stage	gms. (1)	Percent (2)	percent passing (3)	" $\mu$ "
1				16
2				8
3				4
4				2
5				1
6				0.5
Filter				
Total				
Wipe				
Grand Total				

(1) gms = final weight - tare weight

(2) percent = 100% x gms/Total

(3) percent passing ( $n^{\text{th}}$  stage) =  $\sum (n + 1) + (n + 2) + \dots$

For example, percent passing

6th stage = percent filter

2nd stage = percent (Filter + 6<sup>th</sup> + 5<sup>th</sup> + 4<sup>th</sup> = 3<sup>rd</sup>) or  
= percent passing 3<sup>rd</sup> + percent 3<sup>rd</sup>

#### A. Particle Size Distribution

1. Plot "percent passing" vs " $\mu$ " on log - probability paper (see appendix).



6. Turn on the vacuum pump pulling sample through the bypass line.

7. Activate the solenoid valves to obtain a sample for the proper time.

Off gas collectors  
Cooler - 50 sec  
Blower suction  
45 min  
1 min  
40 sec

8. Turn off pump and heater, disassemble apparatus and carefully return the jet injector to the laboratory.

9. Disassemble the jet injector and reweigh the plates and filter paper.

10. Wipe out the cones with a faced tissue and reweigh to obtain the sample that did not adhere to plates or filter.

CALCULATIONS:

First, set up this table:

Stage	gms. (1)	Percent (2)	Percent passing (3)	%
1				10
2				9
3				4
4				2
5				1
6				0.5

Filter  
Total  
Wipe  
Grand Total

(1) gms = final weight - tare weight  
(2) Percent =  $100 \times \text{gms} / \text{Total}$   
(3) Percent passing (n<sup>th</sup> stage) =  $\sum (n + 1) + (n + 2) + \dots$   
For example, percent passing  
6th stage = percent filter  
2nd stage = percent (filter + 6<sup>th</sup> + 5<sup>th</sup> + 4<sup>th</sup> + 3<sup>rd</sup>) or  
= percent passing 3rd + percent 3rd

A. Particle Size Distribution

1. Plot "percent passing" vs "µm on log - probability paper (see Appendix).

2. Draw a straightline through the points.
3. Note the particle size ( $\mu$ ) of the intercepts of this line and the 50% and 84.1% lines.
4. The 50% intercept is the mean particle size,  $D_{mm}$ , in microns,  $\mu$ .
5. The ratio of the 84.1% and 50% intercepts is the particle size deviation,  $\sigma_g$  (dimensionless).

#### B. Mist Loading

$$\text{Mist loading (lb/MSCF)} = 7.904 \times \frac{\text{Grand Total}}{\text{Time (min)}}$$

#### C. Loss

$$\text{Loss, \%} = 100\% \times \frac{\text{Wipe}}{\text{Grand Total}}$$

Report all values to the nearest tenth;  $D_{mm}$  to 0.1,  $\sigma_g$  to 0.1; Loading to 0.1 lb/MSCF; Loss to 0.1%.

#### NOTE:

- (1) All sampling is done isothermally at 200°F to simplify calculations and to eliminate errors caused by condensation of water vapor. Some losses, due to light end volatilization, may occur.
- (2) Valid mist characterization depends upon isokinetic sampling. For this test it is assumed that the flow in the center of a pipe is 1.2 times the mean flow. The available probe tips permits matching flows within 10%. In addition to requiring matched flow velocities, isokinetic sampling requires lamellar flow. Since the design of the retort and recycle gas system causes turbulent flow, true isokinetic sampling is impossible. This is especially true for the off-gas collector sample.



3. Draw a straightline through the points.
4. Note the particle size ( $\mu$ ) of the intercepts of this line and the 50% and 84.1% lines.
5. The 50% intercept is the mean particle size,  $D_{50}$ , in microns,  $\mu$ .
6. The ratio of the 84.1% and 50% intercepts is the particle size deviation,  $\sigma$  (dimensionless).

#### B. Mist Loading

$$\text{Mist Loading (lb/MSCF)} = 7.304 \times \frac{\text{Grand Total}}{\text{Time (min)}}$$

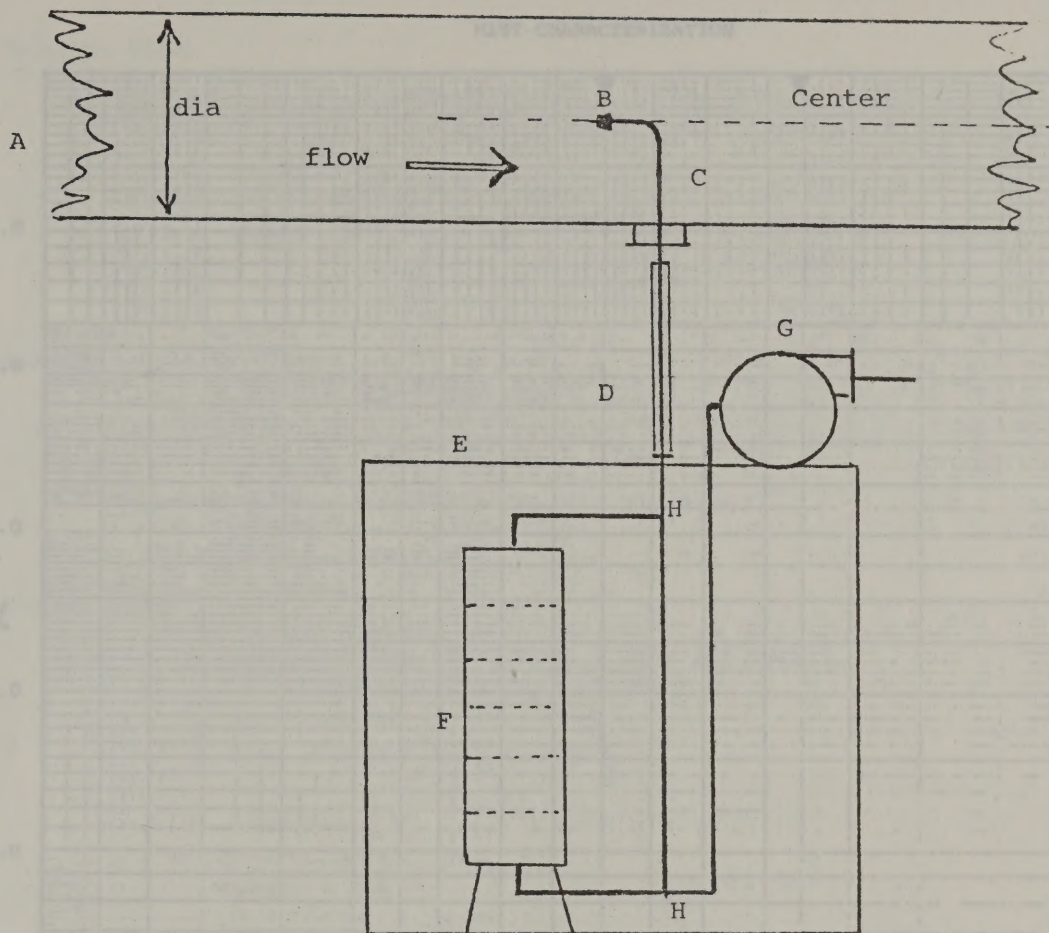
#### C. Loss

$$\text{Loss, \%} = 100 \times \frac{\text{Wipe}}{\text{Grand Total}}$$

Report all values to the nearest tenth;  $D_{50}$  to 0.1,  $\sigma$  to 0.1; Loading to 0.1 lb/MSCF; Loss to 0.1%.

#### NOTE:

- (1) All sampling is done isothermally at 200°F to simplify calculations and to eliminate errors caused by condensation of water vapor. Some losses, due to light end volatilization, may occur.
- (2) Valid mist characterization depends upon isokinetic sampling. For this test it is assumed that the flow in the center of a pipe is 1.5 times the mean flow. The available probe tips generate matching flows within 10%. In addition to repeating matched flow velocities, isokinetic sampling requires laminar flow. Since the design of the test and recycle gas system causes turbulent flow, true isokinetic sampling is impossible. This is especially true for the off-gas collector sample.

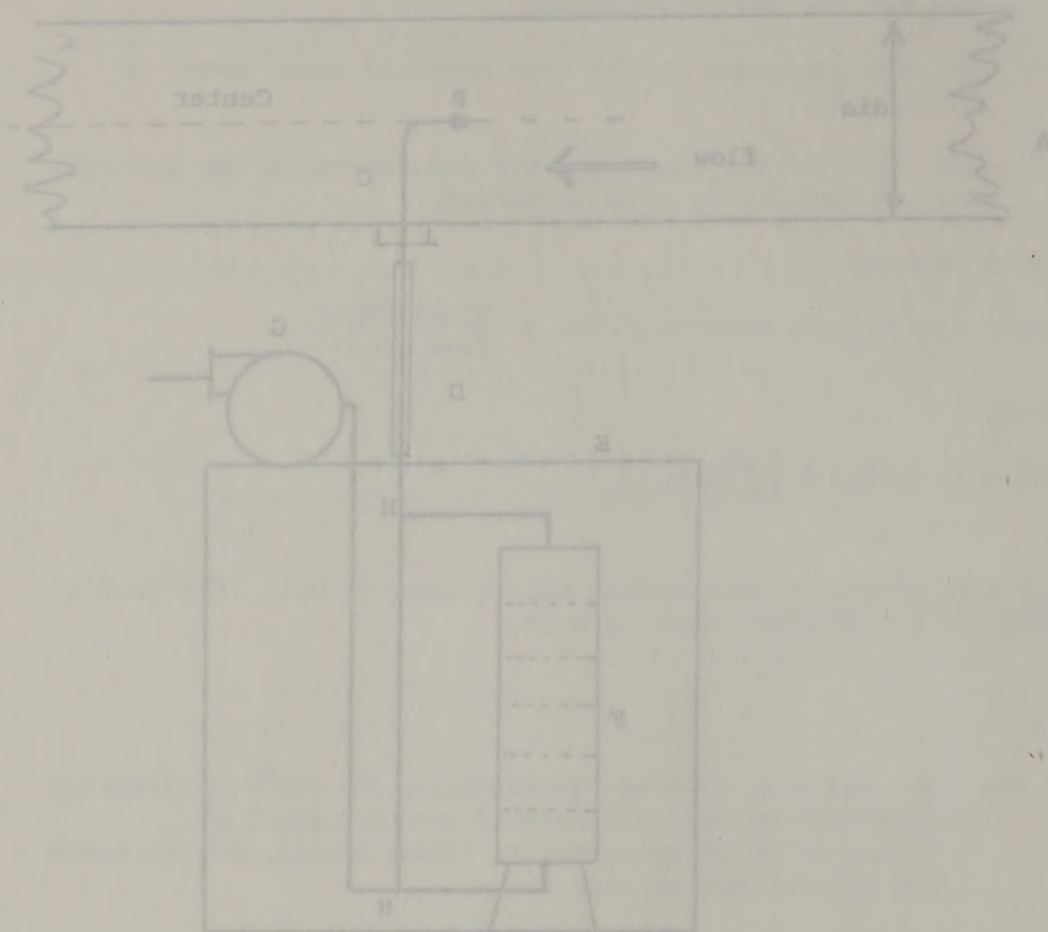


- A Pipe
- B Probe Tip
- C Probe
- D Extension (heated)
- E Impactor Box
- F Cascade Jet Impactor
- G Vacuum Pump
- H Solenoid Valve

Sampling Assembly

Figure 2-5

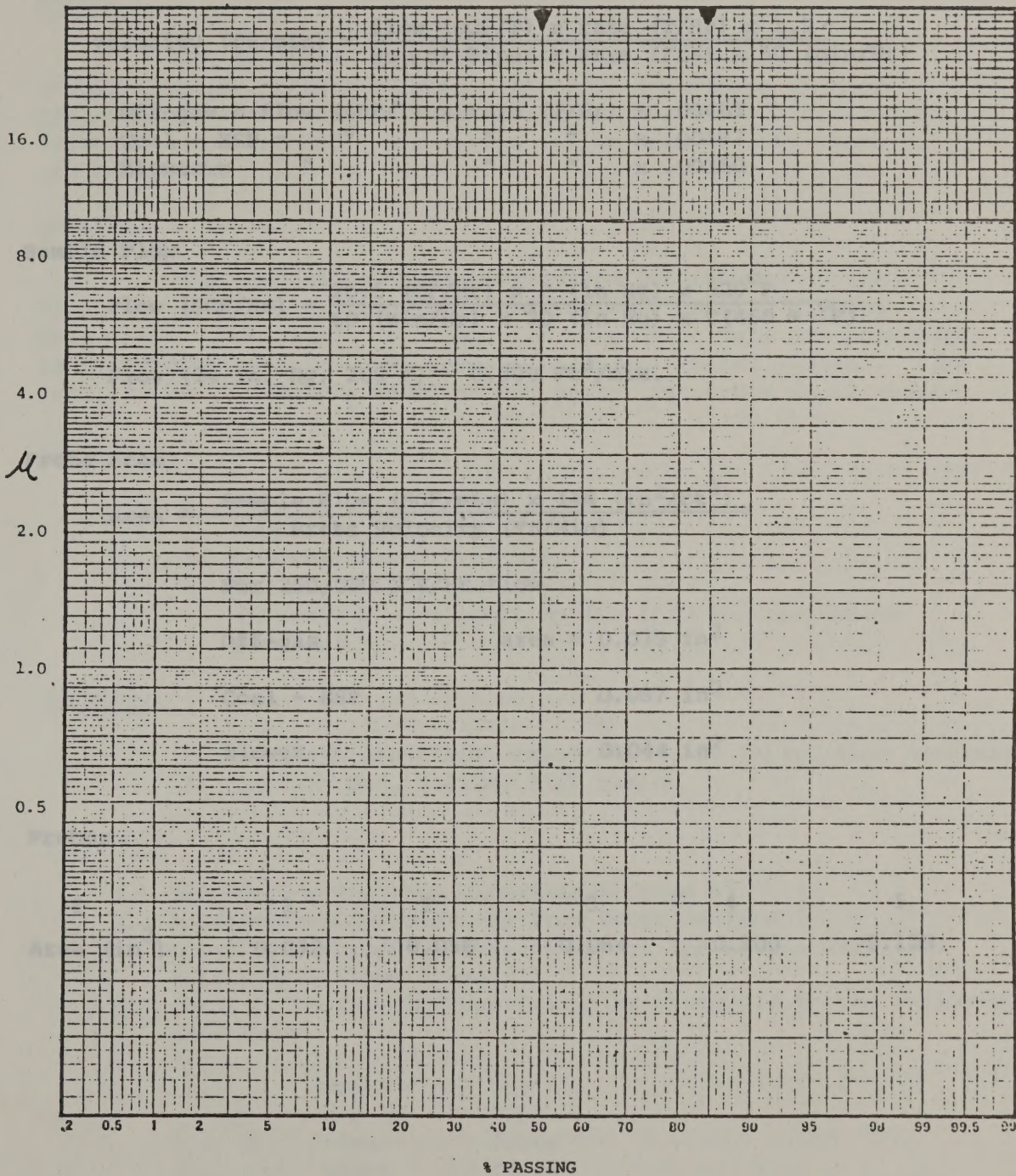




Sampling Assembly  
Figure 3-5

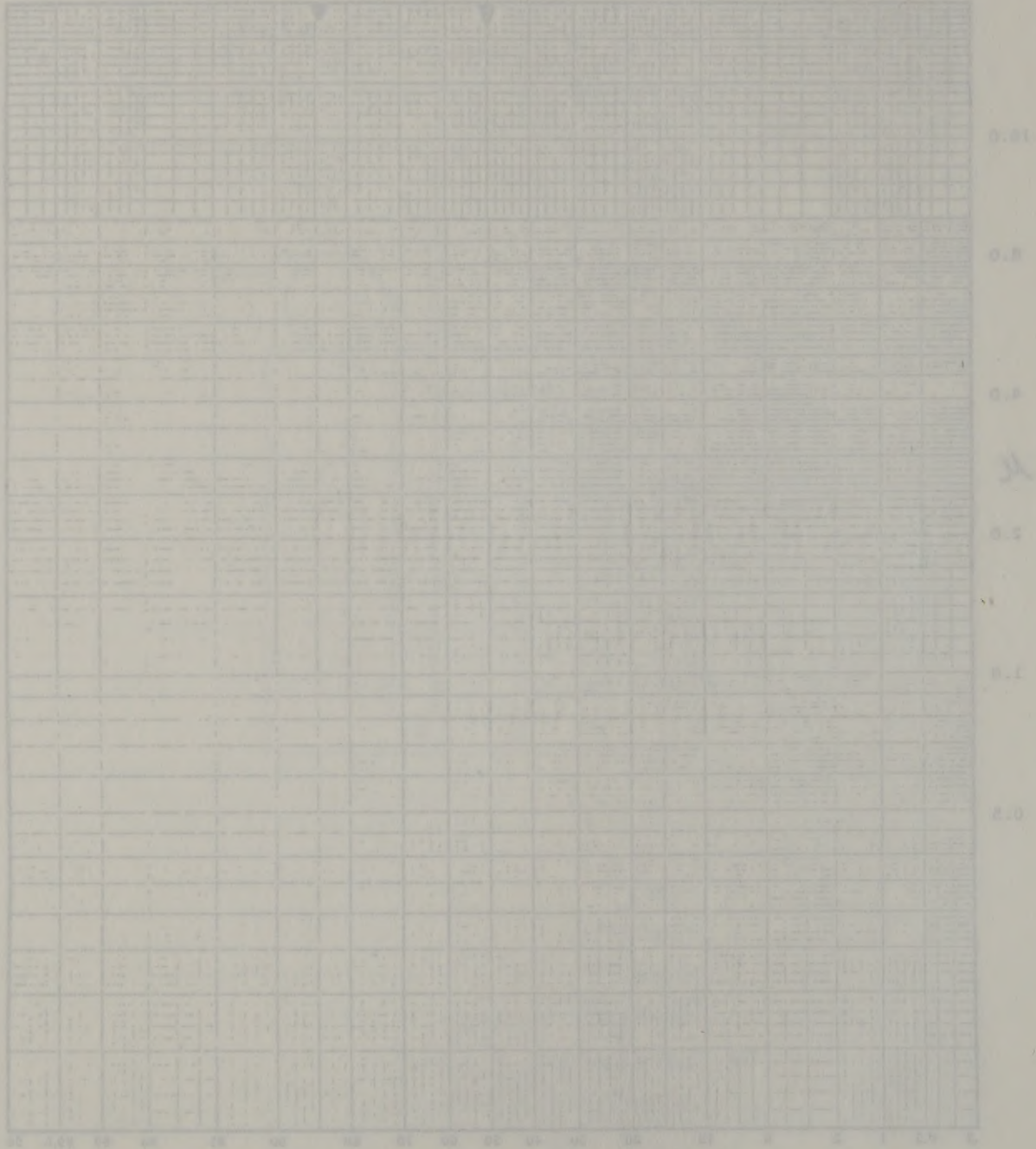
- A Pipe
- B Probe Tip
- C Probe
- D Extension (heated)
- E Inspector Box
- F Cascade Jet Injector
- G Vacuum Pump
- M Solenoid Valve

MIST CHARACTERIZATION





WATER QUALITY DATA



WATER QUALITY DATA

# APPENDIX 2-5

## Probe Tip Calculations

### Process Flow

$$\text{Velocity (ft/min)} = \frac{\text{flow (SCF/T)} \times \text{rate (T/Hr)} \times 1.2}{\text{No. of Pipes} \times \text{Area (Ft}^2) \times 60 \text{ (min/Hr)}}$$

$$\text{Off-gas} = \text{flow (SCF/T)} \times \text{rate (T/Hr)} \times .00463$$

$$\text{Coal - ESP} = \text{ " " " " } \times .00182$$

$$\text{Blower} = \text{ " " " " } \times .00360$$

### Sample Flow

$$\text{Flow (SCF/Hr)} = \frac{26.5 \text{ (CF/Hr)} \times P \text{ (in Hg)} \times 520^{\circ}\text{F}}{60 \text{ (min/Hr)} \times 30 \text{ (in Hg)} \times T(460 + ^{\circ}\text{F})}$$

$$\text{Flow (24 in. Hg, 200}^{\circ}\text{F)} = 0.289 \text{ Ft}^3/\text{min.}$$

### Probe Area

$$\text{area} = \frac{\text{Sample Flow (SCF/min)} \times 144 \text{ (in}^2/\text{Ft}^2)}{\text{Press Velocity (Ft/Min)}}$$

For 250,000 SCF/Hr flow

$$\text{Off-gas} \quad \text{area} = 0.035 \text{ in}^2$$

$$\text{Coal - ESP} \quad 0.087 \text{ in}^2$$

$$\text{Blower} \quad 0.044 \text{ in}^2$$

### Probes

#	1	2	3	4	5
Area (in <sup>2</sup> )	0.032	0.056	0.084	0.100	0.129



# Appendix 1-2

## Probe Tip Calculations

### Process Flow

$$\text{Velocity (ft/min)} = \frac{\text{Flow (SCF/T)} \times \text{Rate (T/hr)} \times 1.2}{\text{No. of Pipes} \times \text{Area (ft}^2\text{)} \times 60 \text{ (min/hr)}}$$

$$\begin{aligned} \text{Off-gas} &= \text{Flow (SCF/T)} \times \text{Rate (T/hr)} \times .00463 \\ \text{Coal} &= \text{Flow (SCF/T)} \times \text{Rate (T/hr)} \times .00182 \\ \text{Blower} &= \text{Flow (SCF/T)} \times \text{Rate (T/hr)} \times .00360 \end{aligned}$$

### Sample Flow

$$\text{Flow (SCF/hr)} = \frac{26.2 \text{ (CF/hr)} \times P \text{ (in Hg)} \times 520^\circ P}{60 \text{ (min/hr)} \times 30 \text{ (in Hg)} \times T(520 + ^\circ P)}$$

$$\text{Flow (34 in. Hg, } 200^\circ P) = 0.288 \text{ ft}^3/\text{min.}$$

### Probe Area

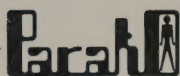
$$\text{Area} = \frac{\text{Sample Flow (SCF/min)} \times 144 \text{ (in}^2\text{ft}^2\text{)}}{\text{Process Velocity (ft/min)}}$$

For 250,000 SCF/hr flow

$$\begin{aligned} \text{Off-gas} & \text{ area} = 0.032 \text{ in}^2 \\ \text{Coal} & \text{ area} = 0.007 \text{ in}^2 \\ \text{Blower} & \text{ area} = 0.044 \text{ in}^2 \end{aligned}$$

### Probes

Area (in <sup>2</sup> )	1	2	3	4	5
0.032	0.007	0.044	0.100	0.138	



## PARAHO OIL SHALE DEMONSTRATION

### On-Stream Gas Chromatograph

#### Method P-G-06

#### SCOPE:

The on-stream GC measures oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, and ethane in recycle gas. Water vapor and heavier hydrocarbons are removed by a water-jacketed condenser and a pre-column filled with DC-200, Chrom P, and Porapak T.

#### OUTLINE:

The components are separated on two columns -- the first 14' packed with Porapak T, the second 3' packed with 5A Mole Sieve. Components are detected using TC. Data are presented as bar graphs relating peak heights to volume (mole) percent. Time required for a complete sampling and analytical cycle is 12 minutes.

#### EQUIPMENT:

1. Process GC.
  2. Sample Panel Board.
  3. Controller and Recorder.
  4. Gas Manifold System.
- (Items 1-3 were built by Sun AMMD for the Paraho process).

#### REAGENTS:

1. Standard Gas Mixes, calibrated (see Table 2-4 for analysis).
2. Carrier Gas, Helium, high purity.

#### PROCEDURE:

1. Set carrier gas (see MAINTENANCE, Step 1).
2. Proceed through "Start-up from Power Failure."
3. After temperature reaches 70°C, set the sample flow (see Maintenance Steps 1 and 2.)
4. Check to be sure the Controller switches are in the following positions:

- |        |        |
|--------|--------|
| Power  | "up"   |
| Heater | "up"   |
| Timer  | "down" |
| Chart  | "down" |
| Spec   | "down" |
| Cont.  | "up"   |



## On-Stream Gas Chromatograph

Method P-C-05

SCOPE:

The on-stream GC measures oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, and ethane in recycle gas. Water vapor and heavier hydrocarbons are removed by a water-jacketed condenser and a pre-column filled with DC-200, Chrom P, and Porapak Q.

OUTLINE:

The components are separated on two columns -- the first is packed with Porapak Q, the second is packed with 2A Mole Sieve. Components are detected using GC. Data are presented as bar graphs relating peak heights to volume (mole) percent. Time required for a complete sampling and analytical cycle is 12 minutes.

EQUIPMENT:

1. Process GC.
  2. Sample Panel Board.
  3. Controller and Recorder.
  4. Gas Manifold System.
- (Items 1-3 were built by Sun AMO for the Parado process).

REAGENTS:

1. Standard Gas Mixes, calibrated (see Table-A for analysis).
2. Carrier Gas, Helium, high purity.

PROCEDURE:

1. Set carrier gas (see MAINTENANCE, Step 1).
2. Proceed through "Start-up from Power Failure".
3. After temperature reaches 70°C, set the sample flow (see MAINTENANCE Steps 1 and 2).
4. Check to be sure the Controller switches are in the following positions:

Power	"up"
Heater	"up"
Flow	"down"
Chart	"down"
Spec	"down"
Cont.	"up"

Note: "Start-up from Power Failure"

The on-stream GC is protected against accidental damage from power failures. After a power failure, the sample flow stops and the controller and recorder stop.

- (1) Check Valve cam (see Table 2-5 and Figure 2-7).  
If necessary, adjust to 45-95.
- (2) Push reset button (located between controller and recorder).

#### MAINTENANCE:

##### 1. Flows

- a. Using a bubble flow meter, adjust proper flow rate:  
Sample; 72-78 cc/min (adjust flow by water level, see Figure 2-6)  
Carrier: 70 cc/min (adjust flow by pressure regulator, see Figure 2-6).

##### 2. Temperature

- a. Using the Trouble Check Switch (Figure 2-7).  
check temperature.
- b. If necessary, adjust to 70°C using the temperature control (Figure 2-7).

##### 3. Window Spacings

- a. When the Valve cam is between 45 and 95, flip "Cont" switch to the "down" position (see Figure 2-7).
- b. Record the cam reading and subtract the valve reading from each of the others. Results should compare with "Cam Settings" in Table 2-5.
- c. Check the window frames by switching chart to "up" position.
- d. If necessary readjust Table 2-5 cam settings.  
Note: A screw, located on the side of each cam controls the window width. This should never need adjusting.

#### CALIBRATION:

1. Turn off sample flow (see Figure 2-6).
2. Introduce standard gas mix (#1 for direct mode, #2 for indirect mode).
3. When the system has equilibrated (the bar graphs from two cycles match), record the concentrations.
4. If concentrations match those given in Table 2-5, proceed to Step 6.



Note: "Start-up from power failure"  
The on-stroke CC is protected against accidental damage from power failures. After a power failure, the sample flow stops and the controller and recorder stop.

- (1) Check Valve can (see Table 1-5 and Figure 1-7). If necessary, adjust to 45-55.
- (2) Push reset button (located between controller and recorder).

#### MAINTENANCE:

##### 1. Flow

- a. Using a bubble flow meter, adjust proper flow rate: Sample, 75-78 cc/min (adjust flow by water level, see Figure 1-6); Carrier, 70 cc/min (adjust flow by pressure regulator, see Figure 1-6).

##### 2. Temperature

- a. Using the Trouble Check Switch (Figure 1-7), check temperature.
- b. If necessary, adjust to 70°C using the temperature control (Figure 1-7).

##### 3. Window Readings

- a. When the Valve can is between 45 and 55, flip "On" switch to the "down" position (see Figure 1-7).
- b. Record the can reading and subtract the valve reading from each of the others. Results should compare with "Can Settings" in Table 1-5.
- c. Check the window frames by switching chart to "up" position.
- d. If necessary readjust Table 1-5 can settings.  
Note: A screw, located on the side of each can controls the window width. This should never need adjusting.

#### CALIBRATION:

1. Turn off sample flow (see Figure 1-6).
2. Introduce standard gas mix (#1 for direct mode, #2 for indirect mode).
3. When the system has equilibrated (the bar graphs rise two cycles each), record the concentrations.
4. If concentrations match those given in Table 1-5, proceed to Step 5.

5. Adjust attenuation settings (see Table 2-5 until the recorded concentrations match those in Table 2-4).
6. Confirm calibration by switching to the other Standard Mix.
7. Turn off all standard flow and turn on the sample (see Figure 2-6).

#### CALCULATION:

No calculation is needed. Bar graph reads directly in volume percent. Care must be taken to use the proper full scale reading for each component (see Table 2-4).

NOTE: The data obtained from the on-stream GC are not normalized. Changes in ambient temperature and pressure will affect the data. The on-stream GC data may not compare well with that obtained by Orsat or Lab GC.

NOTE: Refer to the Sun manual for more details concerning the theory, operation and maintenance of the on-stream GC.



2. Adjust attenuation settings (see Table 2-2) until the recorded concentrations match those in Table 2-4).
3. Continue calibration by switching to the other Standard Mix.
4. Turn off all standard flow and turn on the sample (see Figure 2-6).

CALCULATION:

No calculation is needed. Raw graph reads directly in volume percent. Care must be taken to use the proper full scale reading for each component (see Table 2-4).

NOTE: The data obtained from the on-stream GC are not normalized. Changes in ambient temperature and pressure will affect the data. The on-stream GC data may not compare well with that obtained by Grab or Lab GC.

NOTE: Refer to the 800 manual for more details concerning the theory, operation and maintenance of the on-stream GC.

TABLE 2-4  
Standard Gas Composition

COMPONENT	Std #1 (Vol%)	Std #2 (Vol%)
Oxygen	0.29	0.8
Nitrogen	70.7	18.7
Methane	5.0	19.9
Carbon Monoxide	5.0	14.9
Carbon Dioxide	15.0	29.9
Ethylene	2.0	7.9
Ethane	2.0	7.9

(1) For indirect mode operation set switch to "1" (10 Vol% Full Scale).  
(2) Reset after position 4 (start of second column).  
(3) End of program.



TABLE 3-4  
Standard Gas Composition

COMPONENT	Std #1 (Vol%)	Std #2 (Vol%)
Oxygen	0.29	0.8
Nitrogen	70.7	18.7
Methane	2.0	12.9
Carbon Monoxide	2.0	14.9
Carbon Dioxide	12.0	22.9
Ethylene	2.0	7.9
Ethane	2.0	7.9

TABLE 2-5

Controller and Recorder Settings

<u>Cam Designation</u>	<u>Component</u>	<u>Attenuator Setting</u>	<u>Switch</u>	<u>Recorder Full Scale (Vol%)</u>	<u>Cam Setting</u>
Valve					0
Zero					93
1	O <sub>2</sub>	477 $\pm$ 10	1	5	82
2	N <sub>2</sub>	412 $\pm$ 4	1/10 <sup>(1)</sup>	100 <sup>(1)</sup>	80
3	CH <sub>4</sub>	104 $\pm$ 4	1	50	73
4	CO	371 $\pm$ 6	1	25	67
5	CO <sub>2</sub>	125 $\pm$ 2	1	50	42
6	C <sub>2</sub> H <sub>4</sub>	318 $\pm$ 5	1	20	34
7	C <sub>2</sub> H <sub>6</sub>	669 $\pm$ 10	1	10	27.5
8	(2)				48
9	(3)				52.5

- (1) For indirect mode operation set switch to "1" (10 Vol% Full Scale).  
 (2) Rezero after position 4 (start of second column).  
 (3) End of program.



(3) Key of problem.

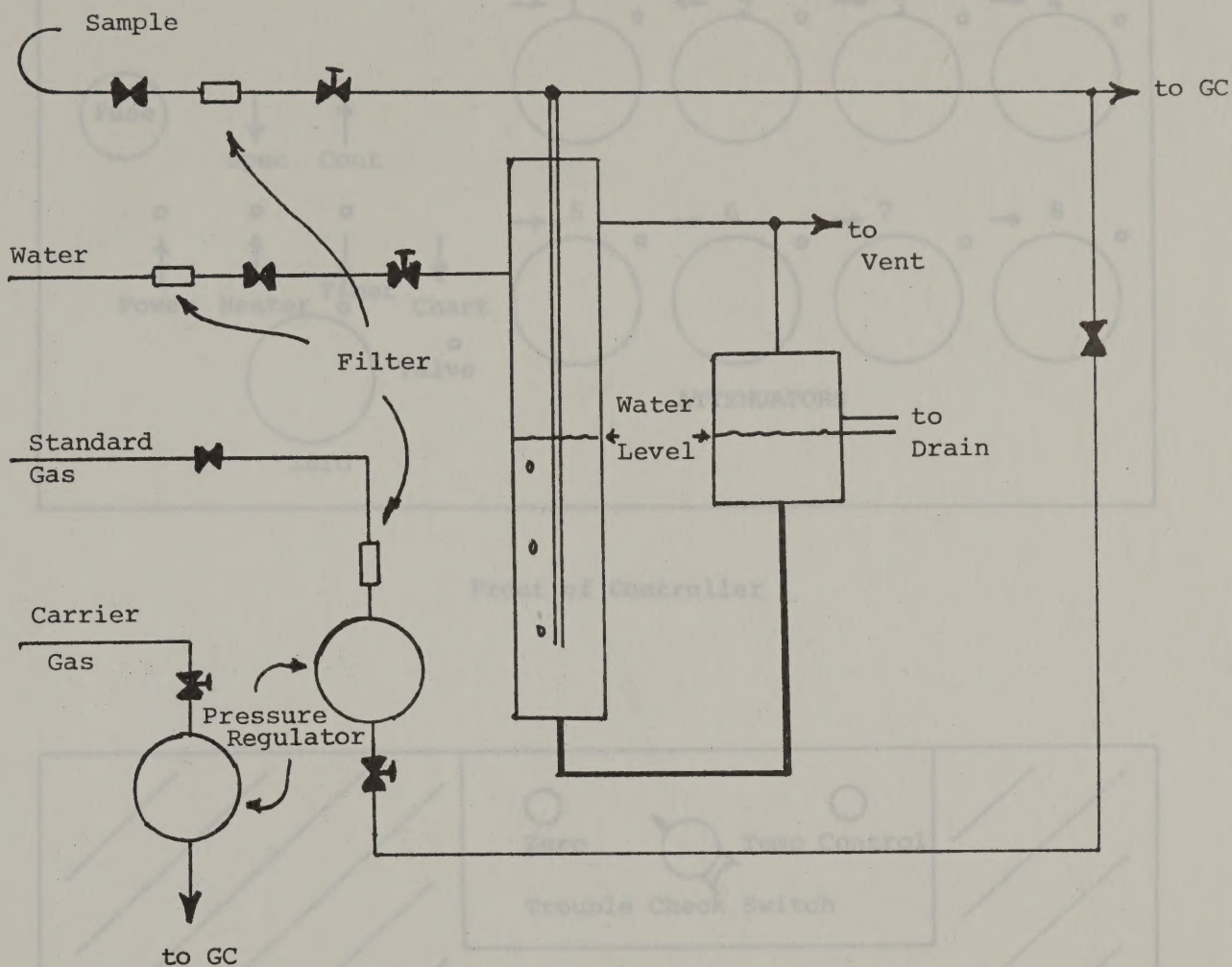
(3) Record after position 4 (start of second column).

(1) Key indicates mode operation per switch to "1". (10 A01# 4011 scale).

Designation Can	Component	Setting Microswitch	Switch Position	Scale (A01#) Recorder Int.	Can Setting
0	(3)				25.2
8	(3)				48
1	C5H6	800 + 10	1	10	51.2
9	C5H4	318 + 2	1	30	34
2	CO <sup>3</sup>	132 + 3	1	20	43
4	CO	317 + 0	1	32	61
3	CH <sup>4</sup>	104 + 4	1	20	33
5	H <sup>5</sup>	473 + 4	1/10 (1)	100 (1)	80
1	O <sup>3</sup>	411 + 10	1	2	85
800					83
40140					0

Continued on Recorder Settings

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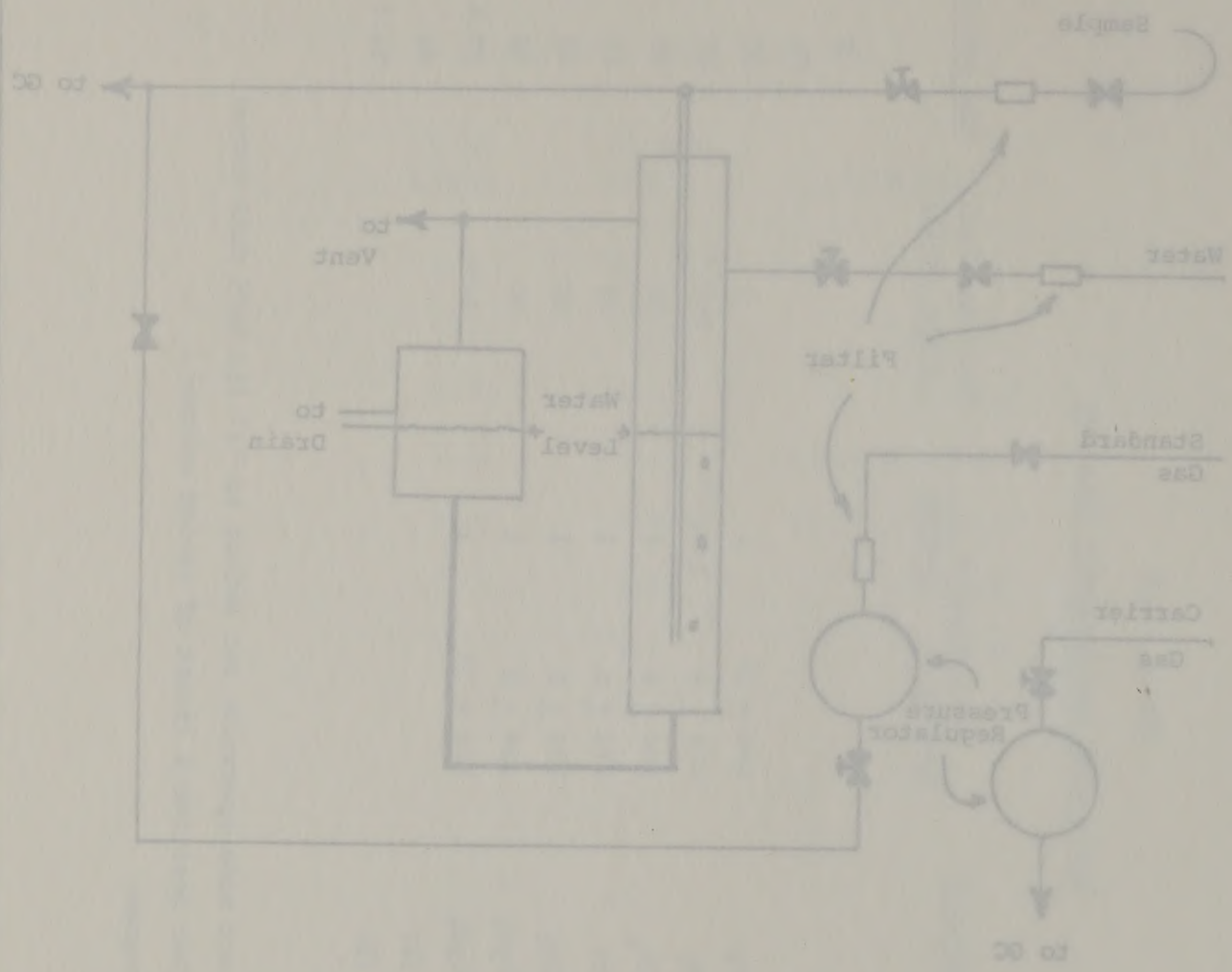


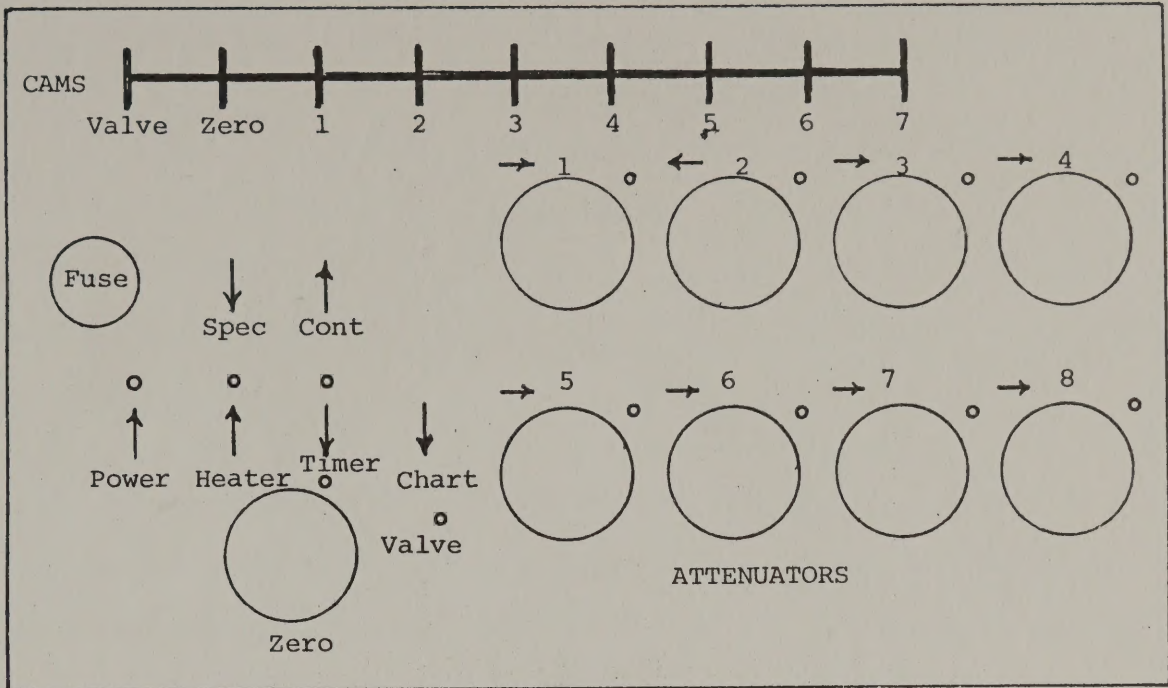
Sample Panel Board

Figure 2-6

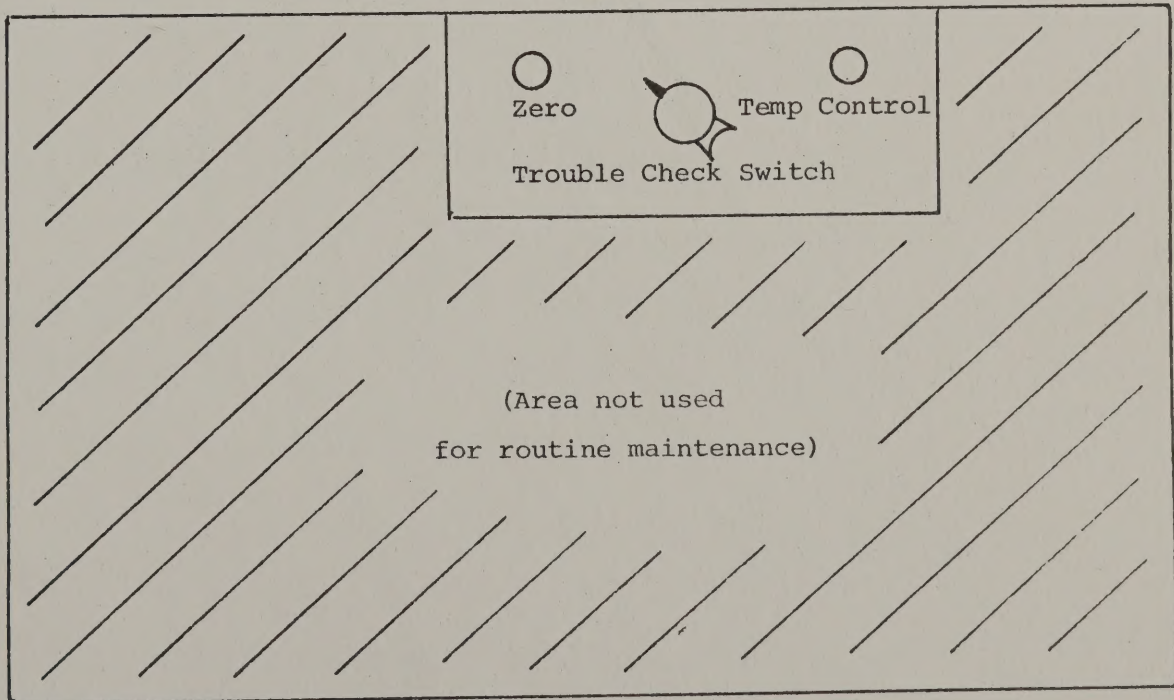


Sample Panel Board  
Figure 3-6



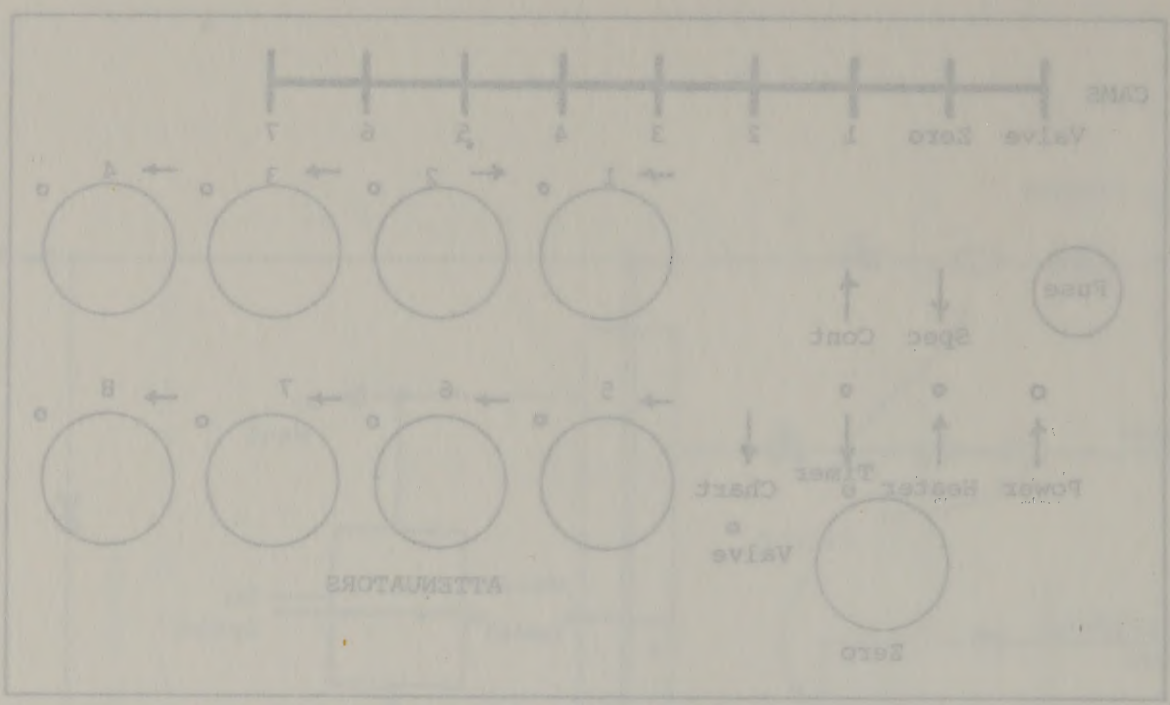


Front of Controller

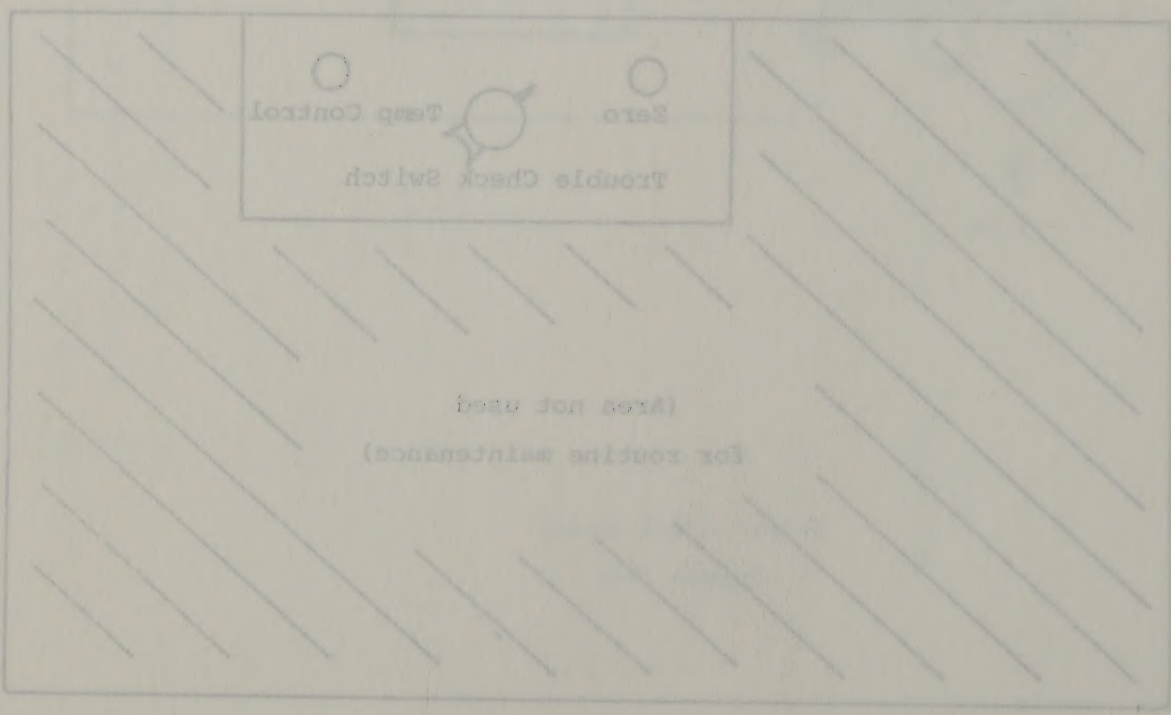


Rear of Controller  
Figure 2-7





Front of Controller



Rear of Controller  
Figure 3-7







### III. SAMPLING

As stated in the SAMPLING memo ... "The success of the Paraho project depends upon obtaining representative samples, good lab results, and valid data interpretation. The importance of the first link in this chain, obtaining representative samples, cannot be overemphasized. It is the basis for everything else that follows."

Although the responsibility for sampling did not fall on the laboratory until the last six months of the project, interest in good sampling practice has always been high. This is evidenced by the D.E.I. memos and notes issued throughout the life of the Paraho project (see Table III-1). Because of the large number of communications regarding sampling, this list may be incomplete. Although this list is used as the basis for this section of the final report, direct references have been avoided. This section is divided into two broad categories -- routine sampling procedures and special sampling procedures.

#### ROUTINE SAMPLING

General. In order to maintain reliable records, a log is kept of all samples taken. If, for some reason, a sample is missed or is taken by non-prescribed means (i.e., a "grab" sample), this information is also listed in the sampling log book.

All samples are tagged promptly with the proper identification:

1. Sample description
2. Retort, run number, and sample number



WESTON BOND

FLUORESCENT

25% COTTON FIBER

3. Date and time

4. Sampler's initials and comments (when applicable)

Sampling schedules are prepared with the cooperation of Data Handling, Laboratory, and Operations so that sufficient data are obtained, laboratory scheduling is maintained and disruptions to operations are kept at a minimum. The sampling schedule insures that overall data reflect overall operations; samples are not missed because operations are not smooth.

Raw Shale. The raw shale sampling system (see Figure III-A-1) obtains a representative 1000-lb sample of raw shale fed to the retort during an 8-hour sampling period and reduces it to 4 lb. of -1/4" sample for laboratory analysis. From January to April 1975, extensive testing, made on the raw shale sampling system, assures that the laboratory sample is representative of the 1000-lb gross sample (see Table III-A-1). Analysis of variance (ANOVA) of the mean Fischer assay data show no bias in Fischer assay oil yield between the two reject samples and the laboratory sample.

The entire sample contained in the lower chute is taken for laboratory analysis. To prevent accidental blockages, the raw shale sampler (feeders and crushers) is run continuously. Some spillage does occur through the flop-gate to the Ty-lab chute. However, studies show that the spillage represented only 0.3% of the gross laboratory sample and the mean Fischer assay oil yield of the material was 26.1 gal/ton. Thus, the amount is small and the analysis does not differ significantly from the raw shale laboratory sample.



# 7. Data and Time

## 4. Sample's Analysis and Comments (when applicable)

Sampling schedule was prepared with the cooperation of Data Analysis, Laboratory, and Operations so that sufficient data are obtained. Laboratory scheduling is maintained and distributed to operations and kept at a minimum. The sampling schedule insures that overall data reflect over all operations; samples are not missed because operations are not working.

### Raw Data. The raw data sampling system (see Figure 11-5-1)

obtains a representative 1000-lb sample of raw shale from the reactor during an 8-hour sampling period and reduces it to 4 lb. of 1/4" sample for laboratory analysis. From January to April 1978, extensive testing was done on the raw shale sampling system. Results show that the laboratory sample is representative of the 1000-lb gross sample (see Table 11-5-1). Analysis of variance (ANOVA) of the mean reactor assay data show no bias in reactor assay of field between the two reactor samples and the laboratory sample.

The reactor sample obtained in the lower chute is taken for laboratory

analysis. To prevent backflow of samples, the raw shale sample

(leakage and moisture) is not representative. Some spillage does occur

through the flap gate on the 15-lb chute. However, results show that the spillage represented only 0.1% of the gross laboratory sample and the mean reactor assay of field of the reactor was 10.1 g/t. Thus, the reactor is well and the analysis does not differ significantly from the raw shale

laboratory sample.

Overall, all tests made during the project indicate that the Paraho raw shale sampling system, consisting of a series of flop-gates, bin, feeders, crushers, and four-stage splitters, does provide an automated, continuous, representative sample for analysis.

Ty-lab screen analysis is performed daily on a grab rather than a composite sample. After clearing the Ty-lab chute of spillage, sufficient sample (about 50 lb.) is taken through the main (upper) flop-gate and diverted to the Ty-lab chute for analysis.

Studies have shown that, unless special equipment is used, the more a sample is ground, the drier it becomes (see Table III-A-2). Thus, the moisture determined in the laboratory (using Method P-S-03 on -100 mesh material) is not a good measure of the surface moisture on raw shale being fed to the retort. Normally, about half the surface moisture on raw shale feed is lost during grinding and handling operations. A grab sample (2-3 lb) of the raw shale feed is taken during each 8-hour sampling period in a sealed metal can for the determination of raw shale moisture (Method P-S-09).

Retorted Shale. The retorted shale sampling system is similar to the raw shale sampling system except that only one crusher and a single 7-stage splitter is used. About 750 lb. of the retorted shale, discharged from the retort during an 8-hour sampling period, is reduced to about a 6 lb sample of -10 mesh material for laboratory analysis. Oxidation of the retorted shale occurs when warm shale is stored in the primary sample hopper for the 8-hour sampling period. Significant difference (as much as 0.3 wt%



Overall, all tests made during the project indicate that the Parana raw shale sampling system, consisting of a series of flip-pates, bins, feeders, crushers, and four-stage splitters, does provide an automated, continuous, representative sample for analysis.

Ty-lab screen analysis is performed daily on a grab rather than a composite sample. After clearing the Ty-lab chute of spillage, sufficient sample (about 50 lb.) is taken through the main (upper) flip-pate and directed to the Ty-lab chute for analysis.

Studies have shown that, unless special equipment is used, the more a sample is ground, the better it becomes (see Table III-A-1). Thus, the moisture determined in the laboratory (using Method E-3-03 on -100 mesh material) is not a good measure of the surface moisture on raw shale being fed to the reactor. Normally, about half the surface moisture on raw shale feed is lost during grinding and handling operations. A grab sample (5-7 lb) of the raw shale feed is taken during each 8-hour sampling period in a sealed metal can for the determination of raw shale moisture (Method E-3-03).

Retorted Shale. The retorted shale sampling system is similar to the raw shale sampling system except that only one crusher and a single 7-stage splitter is used. About 750 lb. of the retorted shale, discharged from the reactor during an 8-hour sampling period, is reduced to about a 5 lb sample of -10 mesh material for laboratory analysis. Oxidation of the retorted shale occurs when raw shale is stored in the primary sample hopper for the 8-hour sampling period. Significant differences (as much as 0.3 wt

organic C) were noted between retorted shale samples grabbed from the belt and sealed in metal cans and those obtained through the normal retorted shale sampling system. However, when the shale leaving the retort is below 400°F and the sampling system (feeder and crusher) is operated continuously, the heat is dissipated and no oxidation occurs. Differences between the grab and continuously ground retorted shale samples taken 1-27-76 averaged -0.02% organic carbon.

Thus, as in the case of raw shale, the sampling system is operated continuously and the entire accumulated sample is taken at the prescribed time during the 8-hour sample period. Single grab samples of retorted shale should be avoided since it is extremely difficult to obtain a representative sample.

Shale Oil. The sampling system (see Figure III-A-2) is quite simple. The oil flows into run-down tanks where it is gauged hourly. After the final gauging in the 8-hour sampling period, the oil flow is diverted to a second tank and the oil in the first tank is agitated and recirculated for 90 minutes. A sample is taken at the discharge of the recirculation pump. While continuing the agitation, the oil is transferred completely to storage tanks. With this procedure, representative oil samples are obtained and no BS & W heel is left to contaminate the succeeding sample.

The validity of the oil sample is best illustrated by the water data (Method P-O-3). Differences between duplicate samples averaged 1.72 wt% water for the period 1-21-76 to 1-25-76. When all sampling procedures were followed (1-26-76 to 2-2-76), the mean difference dropped to 0.25 wt%



organic C) were noted between reformed shale samples grabbed from the belt and sealed in metal cans and those obtained through the normal reformed shale sampling system. However, when the shale leaving the reformat is below 100°F and the sampling system (feeder and crusher) is operated continuously, the heat is dissipated and no oxidation occurs. Differences between the grab and continuously ground reformed shale samples taken 1-17-76 averaged -0.03% organic carbon.

Thus, as in the case of raw shale, the sampling system is operated continuously and the entire accumulated sample is taken at the prescribed time during the 8-hour sample period. Single grab samples of reformed shale should be avoided since it is extremely difficult to obtain a representative sample.

Shale Oil. The sampling system (see Figure III-A-2) is quite simple. The oil flows into run-down tanks where it is gauged hourly. After the final gauging in the 8-hour sampling period, the oil flow is diverted to a second tank and the oil in the first tank is agitated and recirculated for 90 minutes. A sample is taken at the discharge of the recirculation pump. While continuing the agitation, the oil is transferred completely to storage tanks. With this procedure, representative oil samples are obtained and no 82 & W fuel is left to contaminate the succeeding sample.

The validity of the oil sample is best illustrated by the water data (Method 2-O-1). Differences between duplicate samples averaged 1.7% wt water for the period 1-21-76 to 1-25-76. When all sampling procedures were followed (1-26-76 to 2-2-76), the mean difference dropped to 0.15 wt

water. Sampling according to ASTM D-270 shows that both water and sediment will settle out in unstirred tanks (see Table III-A-3). These data show that thorough agitation and bottom-to-top recirculation are needed to obtain valid, representative oil samples.

Recycle Gas. The recycle gas sampling system is shown in Figure III-A-3. Sample loop lines were taken from the recycle gas lines from both retorts to the Retort Control Room. The Pilot Plant sample loop line is a jacketed, steam-traced 1 1/4" line starting from the blower discharge and ending at the blower suction. A similar line had been installed for the Semi-Works but it was changed because of erratic flows, condensation and plugging. The Semi-Works sample loop line, as shown in Figure III-A-3, is a jacketed, steam-traced 1 1/2" line. In order to keep this line as short and straight as possible, it was started at the discharge side of the blower just before the product gas control valve and ended in the thermal oxidizer. The gas sampling system inside the Retort Control Room (see Figure III-A-3) provides for the continuous analysis of Teledyne oxygen and ambient condensate (Method P-G-02), laboratory GC (Method P-G-01) and on-stream GC (Method P-G-06) of the recycle gas from either retort. Simultaneous sampling of recycle gas from both retorts can be done at the Orsat taps.

Several studies were made to assure the validity of the samples taken in the Retort Control room by comparing with samples taken directly from the recycle gas line. Comparisons for laboratory GC data, ambient and sub-ambient condensates, and ammonia and hydrogen sulfide are given in Table III-A-4. In general, samples of recycle gas suffer from the fact that



water. Sampling according to ASTM D-376 shows that both water and sediment will settle out in unfiltered tanks (see Table III-A-3). These data show that thorough agitation and bottom-to-top recirculation are needed to obtain valid representative oil samples.

Recycle Gas. The recycle gas sampling system is shown in Figure III-A-3. Sample loop lines were taken from the recycle gas lines from both returns to the Reactor Control Room. The Pilot Plant sample loop line is a jacketed, steam-traced 1 1/4" line starting from the blower discharge and ending at the blower suction. A similar line had been installed for the East-West but it was changed because of erratic flow, condensation and plugging. The West-West sample loop line, as shown in Figure III-A-3, is a jacketed, steam-traced 1 1/2" line. In order to keep this line as short and straight as possible, it was started at the discharge side of the blower just before the product gas control valve and ended in the thermal oxidizer. The gas sampling system inside the Reactor Control Room (see Figure III-A-3) provides for the continuous analysis of recycle oxygen and ambient methane (Method P-2-02), laboratory GC (Method P-2-03) and on-stream GC (Method P-2-04) of the recycle gas from either reactor. Simultaneous sampling of recycle gas from both reactors can be done at the same time.

Several studies were made to assure the validity of the samples taken in the Reactor Control Room by comparing with samples taken directly from the recycle gas line. Comparisons for laboratory GC data, ambient and sub-ambient condensates, and ammonia and hydrogen sulfide are given in Table III-A-4. In general, samples of recycle gas taken from the fact that

they are grab samples. Composite samples or continuous sampling would provide a more valid picture of the operations.

Although it may appear to be a composite sample, the laboratory GC sample is essentially a grab sample representing at best the recycle gas composition just before the gas sampling bomb is removed.

Although the condensate sample (Method P-G-02) is a composite sample, it suffers many drawbacks. First, the condensate was designed only to clean up the laboratory GC sample. It was not designed to provide a valid sample of water vapor and heavy naphthas. The condensate sample suffers from errors in measurement of the total gas flow and losses of the condensed liquids. These errors and losses, inherent in sampling the recycle gas condensate, can amount to 10% error (relative).

A continuous stream of recycle gas is sent to the Teledyne Oxygen Analyzer (Model No. 9500-I-20). Using its own condenser system (similar to that shown in Figure III-A-3), the oxygen level, detected using a specific electro-chemical transducer, is recorded continuously for either retort. By using the Teledyne Oxygen Analyzer for one retort and the on-stream GC for the other, it is possible to monitor oxygen in recycle gas continuously for both retorts during simultaneous operations.

The Orsat taps, though available for special gas samples, are used primarily for Orsat samples. The Orsat analyses are used as back-up to the other instrumentation. The Orsat trains were designed to measure oxygen, carbon dioxide, and carbon monoxide in recycle gas.



They are grab samples. Composite samples or continuous sampling would provide a more valid picture of the operations.

Although it may appear to be a composite sample, the laboratory GC sample is essentially a grab sample representing at best the recycle gas composition just before the gas sampling bomb is removed.

Although the condensate sample (Method P-3-02) is a composite sample, it suffers many drawbacks. First, the condensate was designed only to clean up the laboratory GC sample. It was not designed to provide a valid sample of water vapor and heavy hydrocarbons. The condensate sample suffers from errors in measurement of the total gas flow and losses of the condensed liquids. These errors and losses, inherent in sampling the recycle gas condensate, can amount to 10% error (relative).

A continuous stream of recycle gas is sent to the Teledyne Oxygen Analyzer Model No. 9500-1-20. Using its own condenser system (similar to that shown in Figure III-A-2), the oxygen level, detected using a specific electro-chemical transducer, is recorded continuously for either reflow. By using the Teledyne Oxygen Analyzer for one reflow and the on-stream GC for the other, it is possible to monitor oxygen in recycle gas continuously for both reflows during simultaneous operations.

The Orsat apparatus, though available for special gas samples, are used primarily for Orsat analysis. The Orsat analysis are used as back-up to the other instrumentation. The Orsat trains were designed to measure oxygen, carbon dioxide, and carbon monoxide in recycle gas.

The on-stream GC continuously monitors a dry recycle gas stream for  $O_2$ ,  $N_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ , and  $C_2H_6$ .

#### SPECIAL

Mists. Sampling of the recycle gas stream for oil mist was always done by laboratory technicians. Samples were taken at the off-gas collectors near the retort, after the coalescer, after the electrostatic precipitator (ESP), and at the blower discharge. Sampling the blower discharge was discontinued because of possible danger from the line pressure and because there was essentially no oil mist in either the ESP or blower discharge sample. This indicates that the Paraho oil separation equipment is effective and any shale oil found in the blower or down-stream lines is a result of upsets and not normal continuous operations.

Two problems exist in mist sampling. One is obtaining sufficient sample to measure without flooding the cascade impactor. The other, isokinetic sampling, was never attained (particularly at the off-gas collectors) because of the configuration of the off-gas system. Thus, the mist data suffers in part that sampling only approached isokinetic conditions.

Rotary Seal Losses. The rotary seal losses were estimated by measuring the  $CO_2$  (and  $H_2$  + hydrocarbons when possible) in the air surrounding seals. These components do not exist in ambient air but are found in recycle gas. Using a grab sample, the GC data are used to determine the amount of recycle gas in the gas-air mixture outside the rotary seal. In the bottom seal, this mixture is measured in the dust-bag collection system. In the top rotary seal, this mixture is measured in an air-gas stream pumped



The on-stream GC continuously monitors a dry recycle gas stream for  $O_2$ ,  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ , and  $C_3H_8$ .

# SPECIAL

Mists. Sampling of the recycle gas stream for oil mist was always done by laboratory technicians. Samples were taken at the off-gas collectors near the reactor, after the condenser, after the electrostatic precipitator (ESP), and at the blower discharge. Sampling the blower discharge was discontinued because of possible danger from the line pressure and because there was essentially no oil mist in either the ESP or blower discharge sample. This indicates that the Paraho oil separation equipment is effective and any shale oil found in the blower or down-stream lines is a result of upsets and not normal continuous operations.

Two problems exist in mist sampling. One is obtaining sufficient sample to measure without flooding the cascade impactor. The other, isokinetic sampling, was never obtained (particularly at the off-gas collectors) because of the configuration of the off-gas system. Thus, the mist data suffers in part that sampling only approached isokinetic conditions.

## Rotary Seal Losses. The rotary seal losses were estimated by

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from the small hopper above the seal. The rotary seal loss is the recycle gas concentration times the gas-air flow. The flow is measured and using a velometer and pipe diameter measurements.

Hydrogen Sulfide and Ammonia. Because of high water vapor concentrations and the solubility of these gases in the condensed water, these gases could not be sampled using bombs in either wet or dry recycle gas (see Table III-A-4). Instead, impingers filled with specific absorbents (acid for  $\text{NH}_3$ , caustic for  $\text{H}_2\text{S}$ ) were used. Although wet gas is fed to the impingers, normal condensation occurs at that point so that the gas being measured in the wet test meter is dry. All data are reported on a dry basis. Sampling is usually done at the Orsat tap in the Retort Control room.

Stack Sampling. Since the water vapor content in most stack effluents was low (<10%), grab samples were taken. These samples were taken through a 4 ft. length of 1/4" ss tubing into a glass sample bomb using a double-valve squeeze bulb according to the EPA procedures. Sampling was made for GC analysis ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and hydrocarbons),  $\text{NH}_3$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . These data are normally reported on an "as is" or wet basis.

Environmental Water. Ground and surface water was sampled from wells and the creek situated in the gulch east of the retorted shale disposal area. Dip samples were taken in plastic containers. Plastic sample bottles (liquid full) were bussed to Rocky Mountain Technology so that analyses were started within 12 hours after the samples were taken.



from the small bag over the seal. The rotary seal loss is the recycle gas concentration times the gas-air flow. The flow is measured and using a velocimeter and pipe diameter measurements.

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# Stack Sampling. Since the water vapor content in most stack

effluents was low ( $<10\%$ ), grab samples were taken. These samples were taken through a 4 in. length of 1/4" ss tubing into a glass sample bomb using a double-valve apparatus built according to the EPA procedures. Sampling was made for GC analysis ( $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ , and hydrocarbons),  $\text{NH}_3$ ,  $\text{NO}_x$ ,  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . These data are normally reported on an "as is" or wet basis.

# Environmental Water. Ground and surface water was sampled from

wells and the creek situated in the ditch east of the retorted shale disposal area. Dip samples were taken in plastic containers. Plastic sample bottles (labeled full) were passed to Rocky Mountain Technology so that analyses were started within 12 hours after the samples were taken.

Grate Samples. Samples of retorted shale were taken directly off the bottom of the grate mechanism. Ten samples, taken across each grate and sealed in metal cans, gave a cross-sectional pattern of the retorted shale leaving the retort. Analysis of these samples for sieve size, benzene solubles, and routine shale tests indicated that no differences occurred. The retorted shale cross-section was quite uniform. Various analyses between differing sieve sizes was also quite uniform; no difference in the retorting reactions with shale size was noted.

Retort Heaters. Sampling of the semi-works heater during the last six months of the project accounted for much of the special sampling increase. This sampling fell into three categories: heater process gas; heater stack gas, and deposits.

The hot process gas was sampled before and after passing through the heater. Samples were taken in evacuated steel bombs that had been nitrogen purged. Leads to the differential manometer served as sample points. GC analysis of the gas samples indicated no discernable differences in hydrogen or hydrocarbon composition between the two samples. Thus cracking reactions within the heater probably were minimal.

The heater stack was sampled frequently to determine the extent of leakage of process gas into the heaters. During retorting operations,  $\text{SO}_2$  was measured to indicate leaks. Process gas contained about 3%  $\text{H}_2\text{S}$  and the heater fuel was low-sulfur. During cold testing, with only air on the burner side,  $\text{CO}_2$  was measured to determine leaks. Process gas contained about 25%  $\text{CO}_2$ , and the air, practically none.



Grate Samples. Samples of retorted shale were taken directly off the bottom of the grate mechanism. Ten samples, taken across each grate and sealed in metal cans, gave a cross-sectional picture of the retorted shale leaving the retort. Analysis of these samples for sieve size, benzene solubility, and routine shale tests indicated that no differences occurred. The retorted shale cross-section was quite uniform. Various analyses between differing sieve sizes was also quite uniform; no difference in the retorting reactions with shale size was noted.

Retort Heater. Sampling of the semi-work heater during the last six months of the project accounted for much of the special sampling increase. This sampling fell into three categories: heater process gas, heater stack gas, and deposits. The hot process gas was sampled before and after passing through the heater. Samples were taken in evacuated steel bombs that had been nitrogen purged. Leads to the differential manometer served as sample points. GC analysis of the gas samples indicated no discernible differences in hydrogen or hydrocarbon composition between the two samples. Thus cracking reactions within the heater probably were minimal.

The heater stack was sampled frequently to determine the extent of leakage of process gas into the heater. During retorting operations, 50% was measured to indicate leaks. Process gas contained about 1% H<sub>2</sub> and the heater fuel was low-sulfur. During cold testing, with only air on the burner side, CO<sub>2</sub> was measured to determine leaks. Process gas contained about 25% CO<sub>2</sub> and the air, practically none.

TABLE III-1

Deposit samples were obtained from the heaters when they were shut down for repairs. Deposits were scraped from normal and ruptured tubes and tube sheets. Depending upon when and where the samples were taken, the following materials were identified: oil, coke, iron scales, sulfides.

Shale fines were not identified in the deposits.

"Moisture on Raw Shale"	12-10-75
"Grate Analysis"	3-13-75
"Raw Shale Sampling System"	1-24-75
"Rotary Seal Loss"	5-1-75
"Heater Deposits"	6-2-75
"Sampling"	9-13-75
"Sampling Update"	9-30-75
"Raw Shale Sampling"	10-20-75
"Recycle Condensates"	11-3-75
"Sampling Operations"	11-3-75
"Retorted Shale Sampling"	11-18-75
"Heater Stack"	12-14-75
"Sampling - Communication and Cooperation"	1-18-76
"Retorted Shale Sampling"	2-2-76
"Dry Ice Condensates"	2-2-76
"Water in Oils"	2-13-76
"Condensate Analysis"	2-26-76
"Water in Oils"	3-10-76
"Heater Stack"	3-10-76



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shut down for repairs. Deposits were scraped from normal and ruptured tubes

and tube sheets. Depending upon when and where the samples were taken, the

following materials were identified: oil, coke, iron scales, sulfides.

These items were not identified in the deposits.

TABLE III-1

DEI SAMPLING MEMOS AND NOTES

"Moisture on Raw Shale"	12-30-74
"Recycle Gas Sampling"	1-6-75
"Grate Analysis"	3-22-75
"Sampling"	3-24-75
"Raw Shale Sampling System"	5-1-75
"Rotary Seal Loss"	6-2-75
"Heater Deposits"	9-12-75
"Sampling"	9-26-75
"Sampling Update"	10-20-75
"Raw Shale Sampling"	11-3-75
"Recycle Condensates"	11-3-75
"Sampling Operations"	11-18-75
"Retorted Shale Sampling"	12-14-75
"Heater Stack"	1-16-76
"Sampling - Communication and Cooperation"	1-18-76
"Retorted Shale Sampling"	2-2-76
"Dry Ice Condensates"	2-2-76
"Water in Oils"	2-13-76
"Condensate Analysis"	2-26-76
"Water in Oils"	3-10-76
"Heater Stack"	3-18-76



TABLE III-1

DEI SAMPLING MEMOS AND NOTES

12-30-74	"Molasses on Raw Shale"
1-6-75	"Acetylene Gas Sampling"
2-12-75	"Grate Analysis"
2-24-75	"Sampling"
2-27-75	"Raw Shale Sampling System"
3-2-75	"Rotary Seal Loss"
3-12-75	"Heater Deposits"
3-26-75	"Sampling"
10-20-75	"Sampling Update"
11-3-75	"Raw Shale Sampling"
11-3-75	"Acetylene Condensates"
11-18-75	"Sampling Operations"
12-14-75	"Reformed Shale Sampling"
1-16-76	"Heater Stack"
1-18-76	"Sampling - Communication and Cooperation"
2-2-76	"Reformed Shale Sampling"
2-2-76	"Dry Ice Condensates"
2-13-76	"Water in Oil"
2-26-76	"Condensate Analysis"
3-10-76	"Water in Oil"
3-18-76	"Heater Stack"

TABLE III-A-1

TABLE III-A-2

PARAHO RAW SHALE SAMPLING SYSTEM STUDY

		"A" (1)	"B" (1)	"C" (1)
1/8/75	FA, oil yield, gal/ton <sup>(2)</sup>	31.02 $\pm$ 1.98	31.6 $\pm$ 1.11	30.4 $\pm$ 0.66
3/24/75	FA, oil yield, gal/ton	26.0 $\pm$ 0.61	27.2 $\pm$ 0.63	26.1 $\pm$ 0.35
4/17/75	FA, oil yield, gal/ton	28.2 $\pm$ 0.32	28.4 $\pm$ 0.77	28.9 $\pm$ 0.55
12-11-74				
12-13-74	Ro-tap, size Dmmd, inches		0.062	0.059
3-10-73				

(1) See figure III-A-1 for sample locations.

(2) Ten replicates, mean  $\pm$  one standard deviation.

(1) No longer used; heat generated during grinding caused drying and possible retorting.



TABLE III-A-1

PERMANENT SHALE SAMPLING SYSTEM STUDY

No-tag, size Twad, inches	FA, oil yield, gal/ton (2)	"A" (1)	"B" (1)	"C" (1)
0.029	28.2 ± 0.32	31.6 ± 1.11	30.4 ± 0.66	
	28.9 ± 0.25	27.2 ± 0.63	26.1 ± 0.32	
	28.4 ± 0.77			

- (1) See figure III-A-1 for sample locations.  
 (2) Ten replicates, mean ± one standard deviation.

TABLE III-A-2

MOISTURE IN RAW SHALE

Water, Wt%						
	Raw Shale Feed (+1/2")	Laboratory Sample (-1/4")	Fischer Assay Sample (-20 mesh)		Regular Sample (-100 mesh)	
Date				Disc Pulverizer		SPEX "Shatterbox"
12-11-74	1.11	0.79	0.71	0.23		
12-15-74	0.56		0.27	0.23		
3-10-75	1.44		0.60	0.19		0.52
3-12-75	0.99		1.17	0.36		0.90
3-14-75	1.40		0.88	0.28 <sup>(1)</sup>		0.85

(1) No longer used; heat generated during grinding caused drying and possible retorting.



TABLE III-A-2  
MOISTURE IN RAW SHALE

Date	Water, Wt%			
	Raw Shale Feed (+1/2")	Laboratory Sample (-1/4")	Fischer Assay Sample (-30 mesh)	Regular Sample (-100 mesh)
12-11-74	1.11	0.79	0.71	0.23
12-12-74	0.56		0.27	0.23
3-10-75	1.44		0.60	0.19
3-12-75	0.99		1.17	0.36
3-14-75	1.40		0.88	0.38 (1)
				SPKX "Shatterbox"
				0.52
				0.90
				0.82

(1) No longer used; heat generated during extruding caused drying and possible retorting.





TABLE III-A-3  
SHALE OIL STORAGE TANKS

SS & W

Depth	Test	200 3-13-78	201 3-15-78	200 3-8-78	% Sediment
Top	0.5	0.48	0.39	Trace	0.34
	2.5	0.19			
Middle	4.5	0.30	0.41	0.19	0.21
	6.5	0.39			
	8.5	0.42			
Bottom	10.0	57.7	23.6	26.2	34.2

TABLE III-A-4

	Concentration, Vol(Mole) %		
	Regular (Condenser)	Orsat Tap (Control Rm)	Recycle Gas Line
GC			
H <sub>2</sub>	4.9	5.1	
		1.2	1.4
N <sub>2</sub>	58.4	58.7	
		65.6	66.3
O <sub>2</sub>	Trace	0.09	
		0.00	0.00
Ar	0.67	0.65	
		0.54	0.53
CO	2.7	2.9	
		2.6	2.7
CH <sub>4</sub>	2.2	2.2	
		2.3	2.3
CO <sub>2</sub>	23.1	23.2	
		25.4	24.1
C <sub>2</sub> H <sub>4</sub>	0.73	0.75	
		0.64	0.63
C <sub>2</sub> H <sub>6</sub>	0.50	0.52	
		0.57	0.57
C <sub>3</sub> H <sub>6</sub>	0.45	0.45	
		0.58	0.57
C <sub>3</sub> H <sub>8</sub>	0.16	0.17	
		0.18	0.19
C-4's	0.20	0.20	
		0.38	0.39
C-5's	Trace	Trace	
		Trace	0.11
Condensate			
Water	19.0	19.1	
	21.4		22.1
Hv. Naphtha	0.40	0.34	
	0.38		0.35



TABLE III-A-4

Concentration, Vol (Mole) %	Regular		Recycle Gas
	(Control Run)	Great Tap	Line
CC			
H <sub>2</sub>	4.9	5.1	1.4
H <sub>2</sub>	28.4	28.7	26.3
O <sub>2</sub>	Trace	0.03	0.00
Ar	0.67	0.62	0.23
CO	2.7	2.9	2.7
CH <sub>4</sub>	2.2	2.3	2.3
CO <sub>2</sub>	23.1	23.2	24.1
C <sub>2</sub> H <sub>6</sub>	0.73	0.75	0.63
C <sub>2</sub> H <sub>4</sub>	0.20	0.22	0.27
C <sub>3</sub> H <sub>8</sub>	0.42	0.42	0.27
C <sub>3</sub> H <sub>6</sub>	0.16	0.17	0.19
C-4's	0.20	0.20	0.39
C-5's	Trace	Trace	0.11
Condensate			
Water	19.0	18.1	22.1
Hy. Hydrocarbons	0.40	0.34	0.35

Table III-A-4 (contd)

RAW SCALE SAMPLING SYSTEM

FIGURE III-A-1

	Regular (Condenser)	Orsat Tap (Control Rm)	Recycle Gas Line
Contaminants			
H <sub>2</sub> S	0.045	0.104	
		1.92	1.80
NH <sub>3</sub>		1.59	1.21

Crusher

Splitters

"X" Sample

Hopper  
Feeder

Crusher

Splitters

Lab Sample - "U" Sample

"X" Sample

Rejects

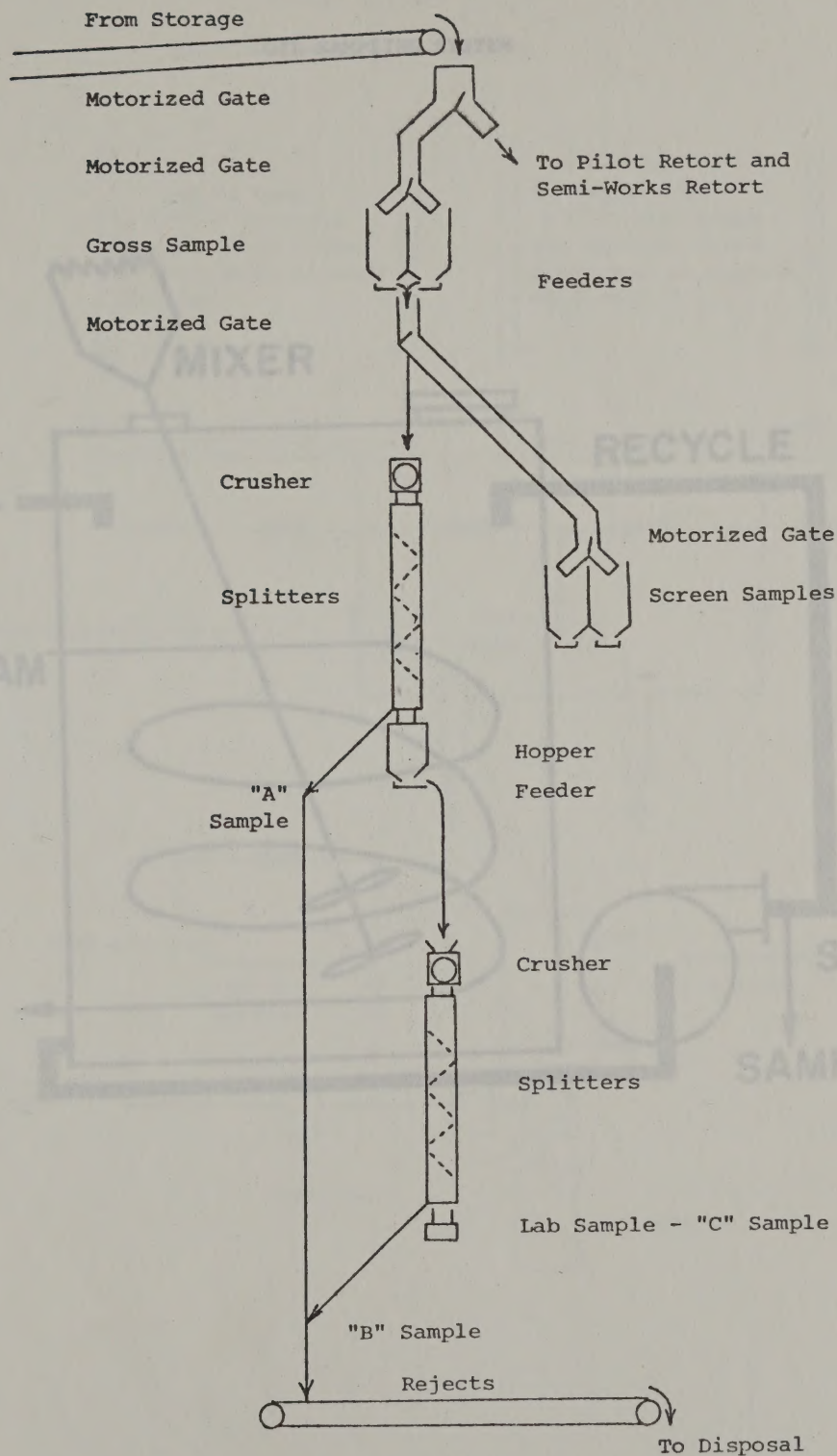
To Disposal





RAW SHALE SAMPLING SYSTEM

FIGURE III-A-1





NEW GRAIN SAMPLING SYSTEM

FIGURE III-A-1

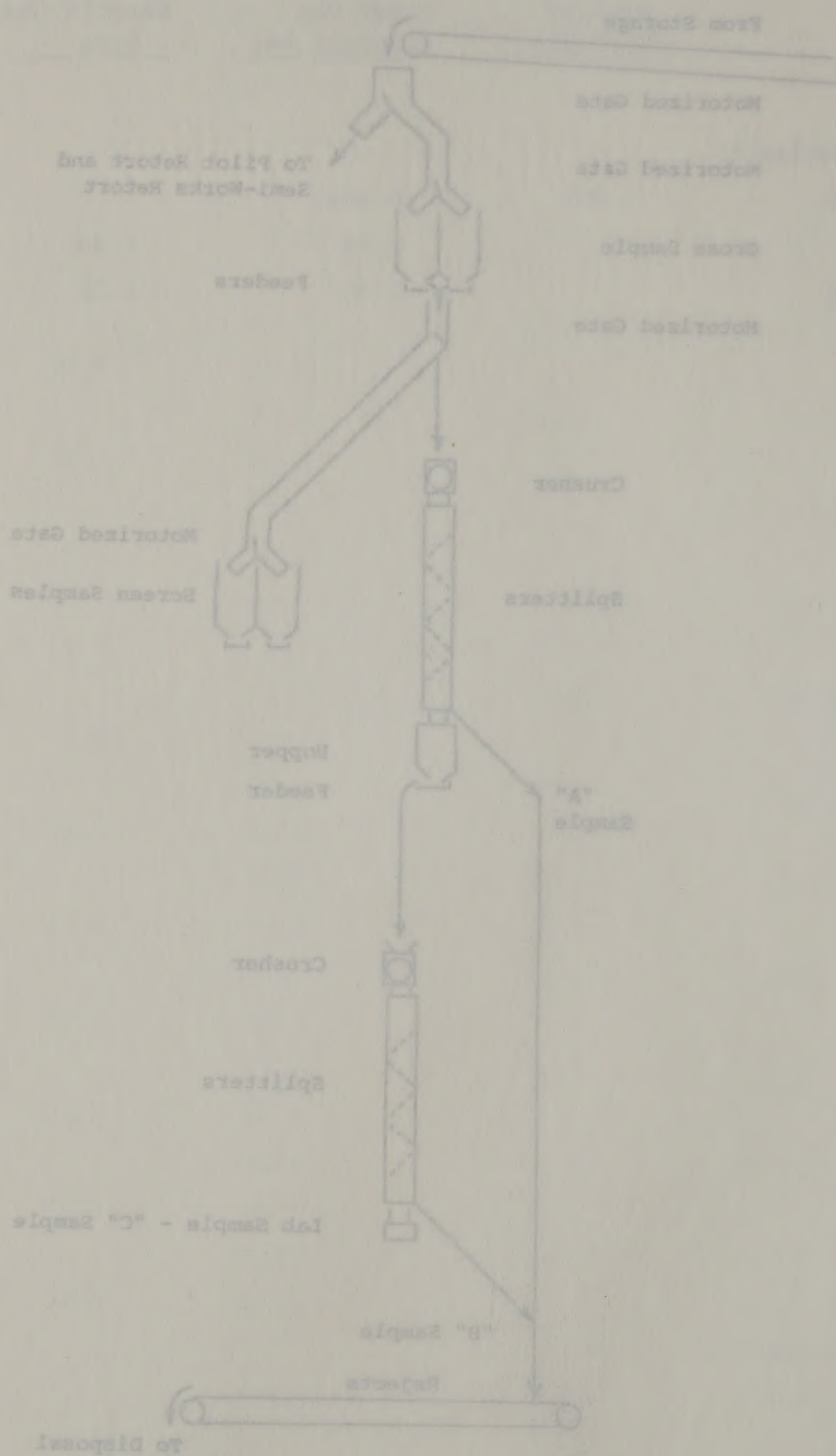


FIGURE III-A-2

OIL SAMPLING SYSTEM

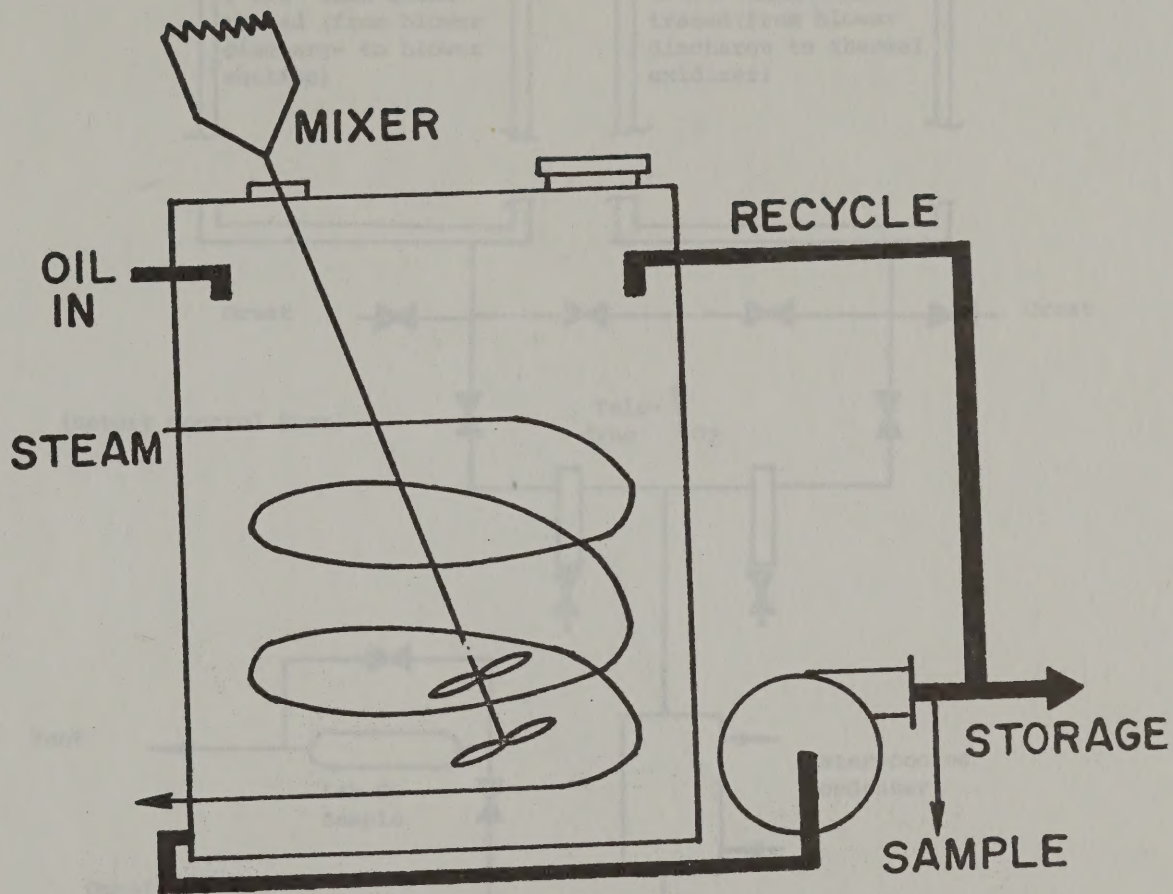




FIGURE 111-A-2

OLD SAMPLING SYSTEM



FIGURE III-A-3

RECYCLE GAS SAMPLING SYSTEM

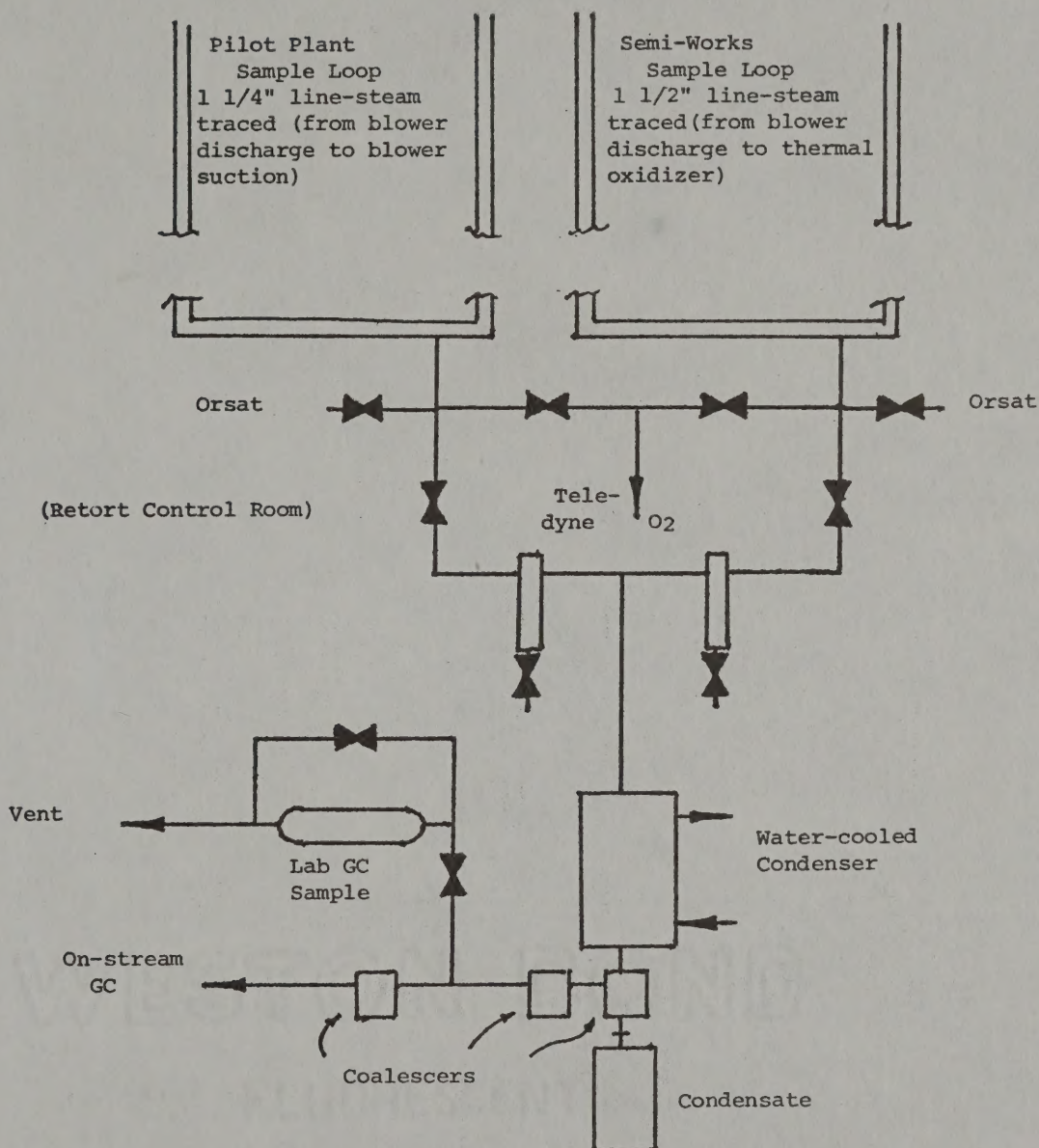
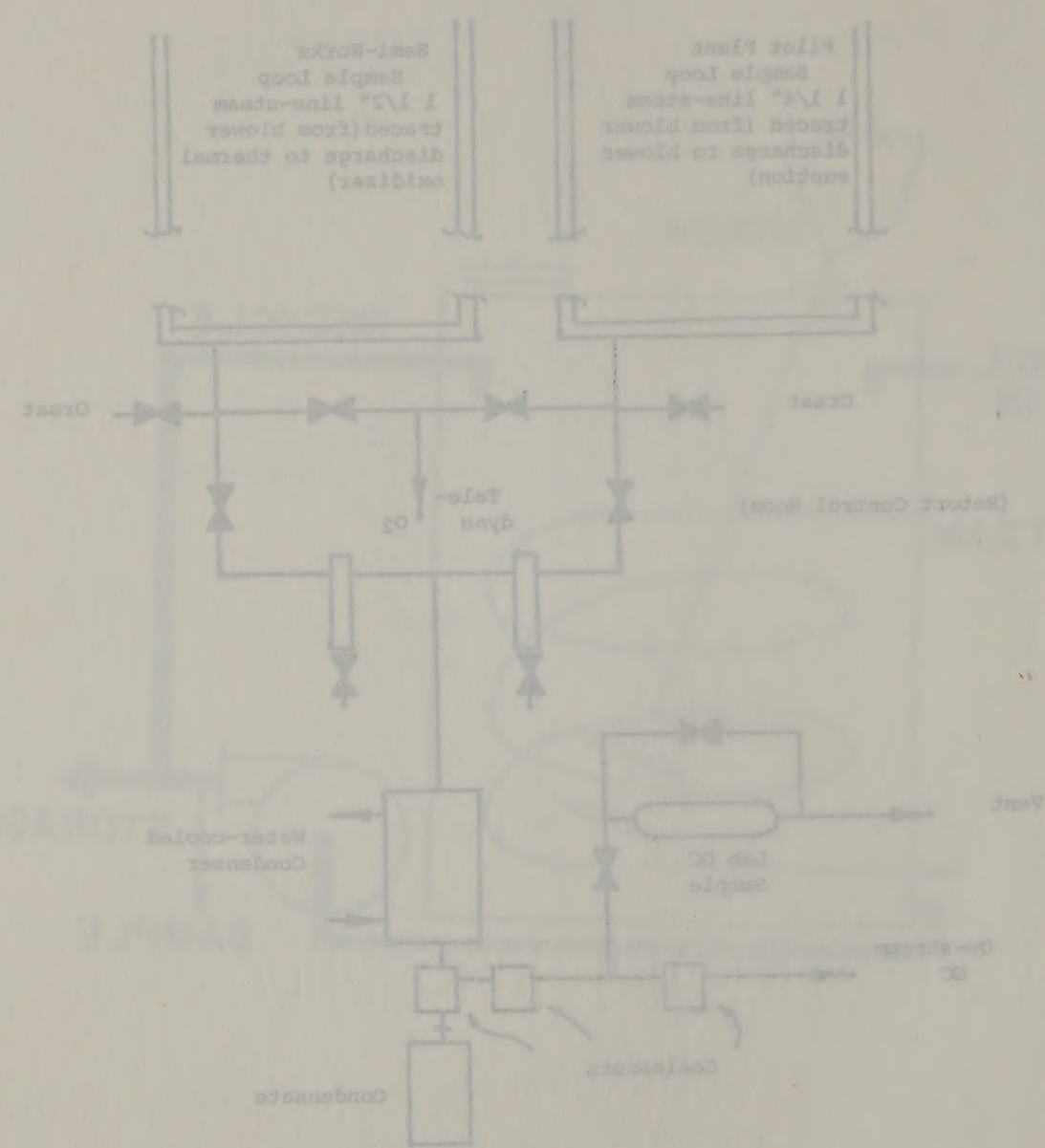




FIGURE III-A-3  
RECYCLE GAS SAMPLING SYSTEM



**4. ENVIRONMENTAL  
TESTING**





#### IV. ENVIRONMENTAL TESTING

More than 3000 test data were obtained by environmental testing during the Paraho project. The environmental testing dealt with the process water (water produced by the retorting process), surface and ground water, and stack emissions. Because of the specialized nature and the sensitivity of these tests, much of the work was performed by outside laboratories.

These laboratories included:

- Rocky Mountain Technology, Golden, Colorado
- Gulf Energy and Minerals Co., Denver, Colorado
- Laramie Energy Research Center, Laramie, Wyoming
- TRW, Redondo Beach, California

#### PROCESS WATER

Because of the nature of the Paraho retorting operation, most of the process water remained as a vapor in the recycle and product gas. Obtaining a sample of water produced with shale oil was quite difficult. Most of the process water analyzed was obtained from oil storage tanks during the project (see Table IV-A-1). Further testing was done in the Paraho laboratory on condensate samples obtained from the recycle gas lines (see Table IV-A-2).

Data from Tables IV-A-1 and 2 show that --

1. Of the cations, only ammonium exceeds 1000 ppm (0.1%) and may have commercial value.
2. Most cations that exhibit toxicity toward plants or animals, if present, are below limits of detection.



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Data from Tables IV-A-1 and 2 show that --

1. Of the cations, only ammonium exceeds 1000 ppm (0.1%) and may have commercial value.
2. Most cations that exhibit toxicity toward plants or animals, if present, are below limits of detection.

3. Four anions (sulfate, nitrate, chloride, and bicarbonate) exceed 1000 ppm (0.1%).
4. Both sulfide and cyanide fall below limits of detection, however, both these anions are quite unstable and can be lost during brief storage.
5. All samples are alkaline and have a disagreeable, characteristic odor.
6. The water-soluble organics vary widely and may depend on many factors: the sample source; pre-treatment (separation) before analysis; the amount of storage, and the type of analysis (COD, BOD, TOC, oil and grease, organic carbon).

#### GROUND AND SURFACE WATER

The monitoring program for ground and surface water was begun in June, 1974 - before any retorting operations had started. The choice of parameters to be tested was made on the basis of elements known to exist in the Piceance Basin from the USBM Bulletin 635 and the experience of Rocky Mountain Technology. Twenty-six parameters were selected. Three additional parameters were added at the suggestions of several participants. The parameters were selected to monitor gross salinity effects, hydrocarbon spills, potential toxins to plant or animal life and miscellaneous (see Table IV-B-1). Sampling was done on a quarterly basis from available sites, the creek, the evaporation pond, and sampling wells. After no changes were noted in the week-by-week data, the weekly samples taken each quarter were stopped.

This report summarizes the data obtained during a two year period.



3. Four anions (nitrate, nitrite, chloride, and bicarbonate) exceed 1000 ppm (0.1%).
4. Both sulfide and cyanide fall below limits of detection, however, both these anions are quite unstable and can be lost during brief storage.
5. All samples are alkaline and have a disagreeable, characteristic odor.
6. The water-soluble organics vary widely and may depend on many factors: the sample source; pre-treatment (separation) before analysis; the amount of storage; and the type of analysis (COD, BOD, TOC, oil and grease, organic carbon).

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This report summarizes the data obtained during a two year period.

Data are presented in graphical form for each of the 29 parameters (Figures IV-B-1 through 29). A map showing the sampling sites is shown in Figure IV-B-30. The following conclusions have been made by Dr. O'Neill (R.M.T.):

1. Most parameters (Si, Kjel N, COD, pH, B, Mo, As, O & G, Cl, Alk, Cd, S. Cu, Pb, Hg, CN, Phos, Na, K, Al, Zn) show little or no change, have no consistent variation, and do not exceed federal or state specifications.
2. Phenols, though variable, and sulfates exceed Colorado drinking water standards.
3. In the stream samples, Total Dissolved Solids and Total Suspended Solids exceed Colorado standards.
4. Iron is highly erratic and often exceeds limits.
5. In the evaporation-retain pond, Cl, As, and Kjel N are high.
6. In Well 4, Ca and Mg exceed Colorado standards.
7. No annual pattern is evident.
8. Since the migration rates of the parameters in the soils at Anvil Points is not known, the monitoring program should be continued to assess long-term impact.

A special study was made in October 1975 sampling several streams from Balzac Gulch (west of mine road) to about four miles to the east (see Figure IV-B-31). These streams flowed adjacent to mine traffic, adjacent to retorting operations (stream D is the same as stream S in the two-year monitoring program), and stream E at least two miles distance from any oil shale activity. Yet the concentrations of their parameters are surprisingly similar (see Table IV-B-2). Statistical analysis of the data shows that



Data are presented in graphical form for each of the 18 parameters (Figures

IV-5-1 through IV-5-18). A map showing the sampling sites is shown in Figure

IV-5-19. The following conclusions have been made by Dr. O'Neill (R.M.T.):

1. Most parameters (Al, Kjel N, COD, Cu, B, Mo, As, O & G, Cl, Alk, Ca, S, Cr, Pb, Hg, Cd, P, Ni, Fe, Zn) show little or no change, have no consistent variation, and do not exceed federal or state specifications.
2. Phenols, though variable, and sulfates exceed Colorado drinking water standards.
3. In the stream samples, Total Dissolved Solids and Total Suspended Solids exceed Colorado standards.
4. Iron is highly variable and often exceeds limits.
5. In the vegetation-soil pairs, Cl, As, and Kjel N are high.
6. In Well 4, Ca and Mg exceed Colorado standards.
7. An annual pattern is evident.
8. Since the migration rates of the parameters in the soils at Well Point is not known, the monitoring program should be continued to assess long-term impact.

A special study was made in October 1975 sampling several streams

from Salinas Gulch (west of mine road) to about four miles to the east (see Figure IV-5-21). These streams flowed adjacent to mine traffic, adjacent to reporting operations (stream 2 is the same as stream 8 in the two-year monitoring program), and stream 3 at least two miles distance from any oil shale activity. Yet the concentrations of their parameters are surprisingly similar (see Table IV-5-2). Statistical analysis of the data shows that

stream D (adjacent and below retorting operations) is not significantly higher than the others and stream E (far removed from any shale processing activities) is not significantly lower than the others.

#### STACK EMISSIONS

Recycle gas data are presented in Table IV-C-1. These data were confirmed by Gulf Energy and Minerals Company, May 5-16, 1975; Rocky Mountain Technology, November 25-26, 1975; TRW, March 6-15, 1976. (Note: copies of the final report of TRW, when received, will be transmitted). The paired data of Table IV-C-1 show that the results obtained by the Paraho laboratory using Method P-G-04 on grab samples are confirmed by reputable outside laboratories using sampling, analyses, and equipment approved by EPA. Thus, it can be concluded that the Paraho data obtained on recycle gas contaminants are reliable.

Stack effluent data were obtained for all stationary sources as required in our lease agreement. These included Boiler Stacks (Table IV-C-2), Thermal Oxidizer (Table IV-C-3) and the Retort External Heaters (Tables IV-C-4 and 5). Data, obtained by outside laboratories, are included whenever applicable. Again, based on comparison of paired data, the Paraho data are reliable. The heater stacks were monitored frequently during the indirect and combination mode runs. The appearance of SO<sub>2</sub> or process gas hydrocarbons in the heater stack effluents indicated process gas leaks in the heaters. These losses, confirmed by process data, caused the thermal oxidizer to operate inefficiently. No thermal oxidizer stack monitoring was done during 1976.



stream D (adjacent and below existing operations) is not significantly higher than the others and stream E (far removed from any shale processing activities) is not significantly lower than the others.

#### STACK EMISSIONS

Recycle gas data are presented in Table IV-C-1. These data were confirmed by Gulf Energy and Minerals Company, May 5-16, 1975; Rocky Mountain Technology, November 25-26, 1975; TSW, March 6-15, 1976. (Note: Copies of the final report of TSW, when received, will be transmitted). The paired data of Table IV-C-1 show that the results obtained by the Paraho laboratory using Method P-6-02 on grab samples are confirmed by reputable outside laboratories using sampling, analyses, and equipment approved by EPA. Thus, it can be concluded that the Paraho data obtained on recycle gas contaminants are reliable.

Stack effluent data were obtained for all stationary sources as reported in our lease agreement. These included Boiler Stack (Table IV-C-2), Thermal Oxidizer (Table IV-C-3) and the Natural Gas Processing Unit (Table IV-C-4 and 5). Data, obtained by outside laboratories, are included whenever applicable. Again, based on comparison of paired data, the Paraho data are reliable. The boiler stacks were monitored frequently during the indirect and combustion mode runs. The appearance of SO<sub>2</sub> or process gas hydrocarbons in the boiler stack effluents indicated process gas leaks in the heaters. These losses, confirmed by process data, caused the thermal oxidizer to operate inefficiently. No thermal oxidizer stack monitoring was done during 1976.

In addition to obtaining paired data with the Paraho laboratory (as shown in Tables IV-C-1 and 3), outside laboratories obtained other data in environmental monitoring. These data are presented in Table IV-C-6.

Overall, the data from Tables IV-C-2 through 6 show that, when stable operations are obtained, composition of the stack effluents are:

Oxygen	6-12 Vol%
Carbon Dioxide	6-12 Vol%
Carbon Monoxide	Not detected (<0.05 Vol%)
Hydrocarbons	Not detected (<0.05 Vol%)
Sulfur Dioxide	0.01-0.02 Vol% (T.O.) (1); <1ppm, others
Oxides of Nitrogen	0.02-0.04 Vol% (T.O.); ~0.01 Vol%, others
Ammonia	0.02-0.03 Vol% (T.O.)
Particulates	$1 \times 10^{-5}$ lb/SCF (dry) (T.O.)
Water Vapor	8-12 Vol% (T.O.)

It has been apparent that continuous monitors should have been used for much of the environmental testing. The important relationship between operating parameters and environmental impact cannot be described in detail. Overall, however, the data do appear to confirm that the Paraho retort is an environmentally acceptable process.

(1) (T.O.) = Thermal Oxidizer



In addition to obtaining tested data with the Paraho laboratory (as shown in Tables IV-C-1 and 2), outside laboratories obtained other data in environmental monitoring. These data are presented in Table IV-C-3.

Overall, the data from Tables IV-C-1 through 3 show that, when stable operations are obtained, composition of the stack effluents are:

Oxygen	8-15 Vol%
Carbon Dioxide	8-15 Vol%
Carbon Monoxide	Not detected (<0.05 Vol%)
Hydrocarbons	Not detected (<0.05 Vol%)
Sulfur Dioxide	0.01-0.02 Vol% (T.O.) (I); <1 ppm, others
Oxides of Nitrogen	0.02-0.04 Vol% (T.O.); <0.01 Vol%, others
Ammonia	0.02-0.03 Vol% (T.O.)
Particulates	$1 \times 10^{-2}$ lb/dry (T.O.)
Water Vapor	8-15 Vol% (T.O.)

It has been apparent that continuous monitoring should have been used for much of the environmental testing. The important relationship between operating parameters and environmental impact cannot be described in detail. Overall, however, the data do appear to confirm that the Paraho reform is an environmentally acceptable process.

(I) (T.O.) = Thermal Oxidizer

TABLE IV-A-1

PARAHO PROCESS WATER SAMPLES

Location	Unknown	Storage Tank	Rundown Tank	Rundown Tank
Date	3/25/75	3/12/75	8/25/75	8/25/75
Analytical Laboratory	LERC	RMT	Gulf	Paraho <sup>(1)</sup>

CATIONS

Aluminum		4.6	2.4	
Ammonium	4910	830	40800	2600
Antimony			<0.9	
Arsenic			<0.005	
Barium			<3	
Boron		10	1.2	
Cadmium		<0.005	<0.9	
Calcium	76	100	18	
Chromium			0.3	
Cobalt			0.15	
Copper		0.04	9	
Iron		2.2	9	7
Lead		0.33	3500	
Lithium			<2	
Magnesium	58	200	30	
Manganese			1.2	
Mercury		<0.06	<0.0001	
Molybdenum		0.43	<0.2	
Nickel			0.2	<2
Potassium	35	18	3	
Silicon		3.5	3	
Silver			0.6	
Sodium	290	140	30	
Strontium			0.6	
Tin			<0.3	
Titanium			<0.2	
Vadadium			<0.3	
Zinc			1.2	

ANIONS

Bicarbonate	1500			
Carbonate	0			
Chloride	5300	1550	70000	13300
Cyanide		<0.001	<0.1	
Fluoride		19	5	
Nitrate			2570	
Nitrite			0.3	
Phosphate		33	<1.5	
Sulfate	5900	210	5500	
Sulfide		<0.001	<0.5	0.5





Table IV-A-1 Cont'd.

Location	Unknown	Storage Tank	Rundown Tank	Rundown Tank
Date	3/25/75	3/12/75	8/25/75	8/25/75
Analytical Laboratory	LERC	RMT	Gulf	Paraho (1)
MISCELLANEOUS				
Ash			300	66
Biol. Oxygen Demand		>5000		
Chem. Oxygen Demand	17000	32000	86400	
Conductivity, M mho/cm			120000	
Kjeldahl Nitrogen	4600	6100	33600	
Oil and Grease		900	964	
pH, units	7.6	8.6	8.4	8.0
Phenol		19	8.7	
Phenolphthalein			620	
Alkalinity (CaCO <sub>3</sub> )				
Threshold Odor			10-20	
Number, units x 10 <sup>-3</sup>				
Total Alkalinity (CaCO <sub>3</sub> )		5900	35200	
Total Diss. Solids	17400	23000	160000	137000
Total Organic Carbon	3420	1060	19300	
Total Sus. Solids	700	11	70	
Total Volatile Solids			159700	137000
Turbidity, JTU			40	

NOTE: All concentrations expressed in mg/l (ppm) unless stated otherwise.

(1) Analyses done after sample was stored several months.





TABLE IV-A-2

## Process Water Analyses

Sample	Oil Separation		Gas Condensation		Condensates <sup>(2)</sup>		Tank 522 <sup>(3)</sup>
Sample No.	Rundown Tank 519		Distributor Lines		A-5	A-9	---
Date	11-14-75	11-16-75	Top 11-10-75	Mid. 11-10-75	3-1-76	3-2-76	3-3-76
pH	9.1	8.4	9.3	9.1			
Total Vol Solids, Wt%	15.82	4.92	0.70	6.67			
Ash, Wt%	0.07	0.04	0.01	0.04			
Elemental							
Total C, Wt%	3.83	2.35	1.48	3.09	2.59	2.06	1.01
Total H, Wt%	10.38	10.82	10.85	10.52	10.59	10.67	11.02
Total N, Wt%	3.35	1.25	1.09	2.01	2.65	2.84	0.97
Min CO <sub>2</sub> , Wt%	2.29	0.23	1.93	1.55	6.27	6.03	0.82
NH <sub>3</sub> , Wt%	0.98	0.47	1.52	1.05	3.22	3.55	0.63
H <sub>2</sub> S, Wt%	0.0002	0.0002	0.0001	0.0002	0.05	0.04	0.02
Mol ratio (NH <sub>3</sub> -N/Min C) <sup>(4)</sup>	0.81	3.86	1.49	1.28	0.97	1.10	1.45
Composition, Wt%							
NH <sub>4</sub> HCO <sub>3</sub>	5.1	1.1	5.3	4.0	12.1	12.1	1.8
(NH <sub>4</sub> ) <sub>2</sub> S	0.0	0.0	0.0	0.0	0.1	0.1	Trace
Soluble oil <sup>(5)</sup>	4.0	2.9	1.2	3.3	1.0	0.5	0.9
Water <sup>(6)</sup>	86.2	93.6	93.4	88.8	82.2	86.9	96.8
TOTAL	95.3	97.6	99.9	96.1	95.4	99.6	99.5

(1) From raw shale oil

(2) Routine samples from Method P-G-02

(3) Rundown from on-line bottom gas cooler

(4) Determined from NH<sub>3</sub> and min CO<sub>2</sub> data. (NH<sub>3</sub>-N/Min CO<sub>2</sub> = 1.0 for NH<sub>4</sub>HCO<sub>3</sub>)

(5) Determined from calculated org C Value.

(6) Determined from total H - ~~2~~ Other H.





TABLE IV-B-1

Ground and Surface Water Parameters

Gross Salinity				(Figure)	
Parameter	Unit	Na	Ca	IV-B-1	Unit
Sodium	Calcium	494	214	-2	125
Potassium	Magnesium	10.5	7.1	-3	3.7
Calcium	Potassium	80.1	79	-4	70.2
Magnesium	Aluminum	96.8	59	-5	65.2
Aluminum	Iron	1.6	3.4	-6	1.4
Iron	Total Dissolved Solids	2.8	1.8	-7	2.5
Zinc	Total Suspended Solids	0.3	0.08	-8	0.13
Chloride	Chloride	828	578	-9	5
Sulfate	Sulfate	37.9	24	-10	11.4
Alkalinity	Phosphate	724	136	-11	432
Total Dissolved Solids	Hydrocarbons	2299	1418	-12	1025
Total Suspended Solids	Oil and Grease	2	9	-13	1
Cadmium	Chemical Oxygen Demand	<0.002	<0.002	-14	<0.002
Copper	Phenols	0.002	0.002	-15	0.03
Lead	Potential Toxins	<0.1	<0.1	-16	<0.1
Mercury	Zinc	0.007	0.005	-17	0.003
Fluoride	Cadmium	2.7	0.5	-18	1.0
Cyanide	Lead	<0.001	<0.001	-19	<0.001
Sulfide	Mercury	<0.05	<0.05	-20	<0.05
Phosphate	Boron	<0.02	0.02	-21	<0.02
Silica (as Si)	Molybdenum	11.0	10.7	-22	14.1
Nitrogen, Kjeldahl	Arsenic	1.8	0.8	-23	<0.2
Oxygen, Chemical	Fluoride	41.5	35.1	-24	12.0
Phenols	Cyanide	0.005	<0.001	-25	0.004
pH	Miscellaneous	8.40	8.16	-26	7.88
Boron	Copper	<0.1	<0.1	-27	<0.1
Arsenic	Sulfide	0.004	0.001	-28	0.001
Molybdenum	Silica (As Si)	2.0	<0.2	-29	<0.2
	Kjeldahl Nitrogen				
	Alkalinity (as CaCO <sub>3</sub> )				
	pH				

NOTE: All samples except pH were analyzed by the State of California Department of Water Resources. Samples were analyzed by the State of California Department of Water Resources. Samples were analyzed by the State of California Department of Water Resources.



TABLE IV-2-1

Ground and Surface Water Parameters

Ground Water Parameters		Surface Water Parameters	
1	PH	1	PH
2	Alkalinity (as CaCO <sub>3</sub> )	2	Alkalinity (as CaCO <sub>3</sub> )
3	Kjeldahl Nitrogen	3	Kjeldahl Nitrogen
4	Si	4	Si
5	SiO <sub>2</sub> (As Si)	5	SiO <sub>2</sub> (As Si)
6	Sulfide	6	Sulfide
7	Copper	7	Copper
Miscellaneous		Miscellaneous	
8	Cyanide	8	Cyanide
9	Fluoride	9	Fluoride
10	Arsenic	10	Arsenic
11	Molybdenum	11	Molybdenum
12	Boron	12	Boron
13	Mercury	13	Mercury
14	Lead	14	Lead
15	Cadmium	15	Cadmium
16	Zinc	16	Zinc
Potential Toxins		Potential Toxins	
17	Phenols	17	Phenols
18	Chemical Oxygen Demand	18	Chemical Oxygen Demand
19	Oil and Grease	19	Oil and Grease
Hydrocarbons		Hydrocarbons	
20	Phosphate	20	Phosphate
21	Sulfate	21	Sulfate
22	Chloride	22	Chloride
23	Total Suspended Solids	23	Total Suspended Solids
24	Total Dissolved Solids	24	Total Dissolved Solids
25	Iron	25	Iron
26	Aluminum	26	Aluminum
27	Potassium	27	Potassium
28	Magnesium	28	Magnesium
29	Calcium	29	Calcium
30	Sodium	30	Sodium
Gross Salinity		Gross Salinity	

(Figure)

IV-2-1

-1

-2

-3

-4

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-12

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TABLE IV-B-2

VARIOUS STREAM SAMPLING DATA  
STREAMS

Parameter	B	C	D	E	F
Sodium	494	214	309	128	125
Potassium	10.5	7.1	23.2	4.2	3.7
Calcium	80.1	79.5	94.4	79.5	70.2
Magnesium	96.8	59.9	65.7	66.8	65.2
Aluminum	1.6	2.0	3.4	2.2	1.4
Iron	2.6	0.3	1.8	0.4	0.5
Zinc	0.05	0.06	0.06	0.06	0.13
Chloride	5	7	93	4	5
Sulfate	828	578	888	422	667
Oil & Grease	37.0	24.4	33.6	37.2	11.4
Alkalinity	734	336	381	336	452
Total Dissolved Solids	2299	1418	1716	1380	1025
Total Suspended Solids	2	9	93	1	8
Cadmium	<0.002	<0.002	<0.002	<0.002	<0.002
Copper	0.02	0.04	0.02	0.02	0.03
Lead	<0.1	<0.1	<0.1	<0.1	<0.1
Mercury	0.007	0.005	0.005	0.004	0.003
Fluoride	2.7	0.6	2.7	0.8	1.0
Cyanide	<0.001	<0.001	<0.001	<0.001	<0.001
Sulfide	<0.05	<0.05	<0.05	<0.05	<0.05
Phosphate (as P)	<0.02	0.03	0.06	<0.02	<0.02
Silica (as SiO <sub>2</sub> )	13.0	10.7	11.1	11.7	14.1
Nitrogen, Kjeldahl	I.S.	0.8	<0.2	I.S.	<0.2
Oxygen, Chemical Demand	41.5	35.1	26.4	22.3	12.8
Phenols	0.005	<0.001	0.002	0.005	0.004
pH	8.40	8.16	8.12	8.01	7.88
Boron	<0.1	<0.1	<0.1	<0.1	<0.1
Arsenic	0.004	0.003	0.003	0.002	0.001
Molybdenum	2.0	<0.2	<0.2	<0.2	<0.2

NOTE: All data are in ppm except pH

I.S. - Insufficient sample remaining to perform determination.



TABLE IV-B-1

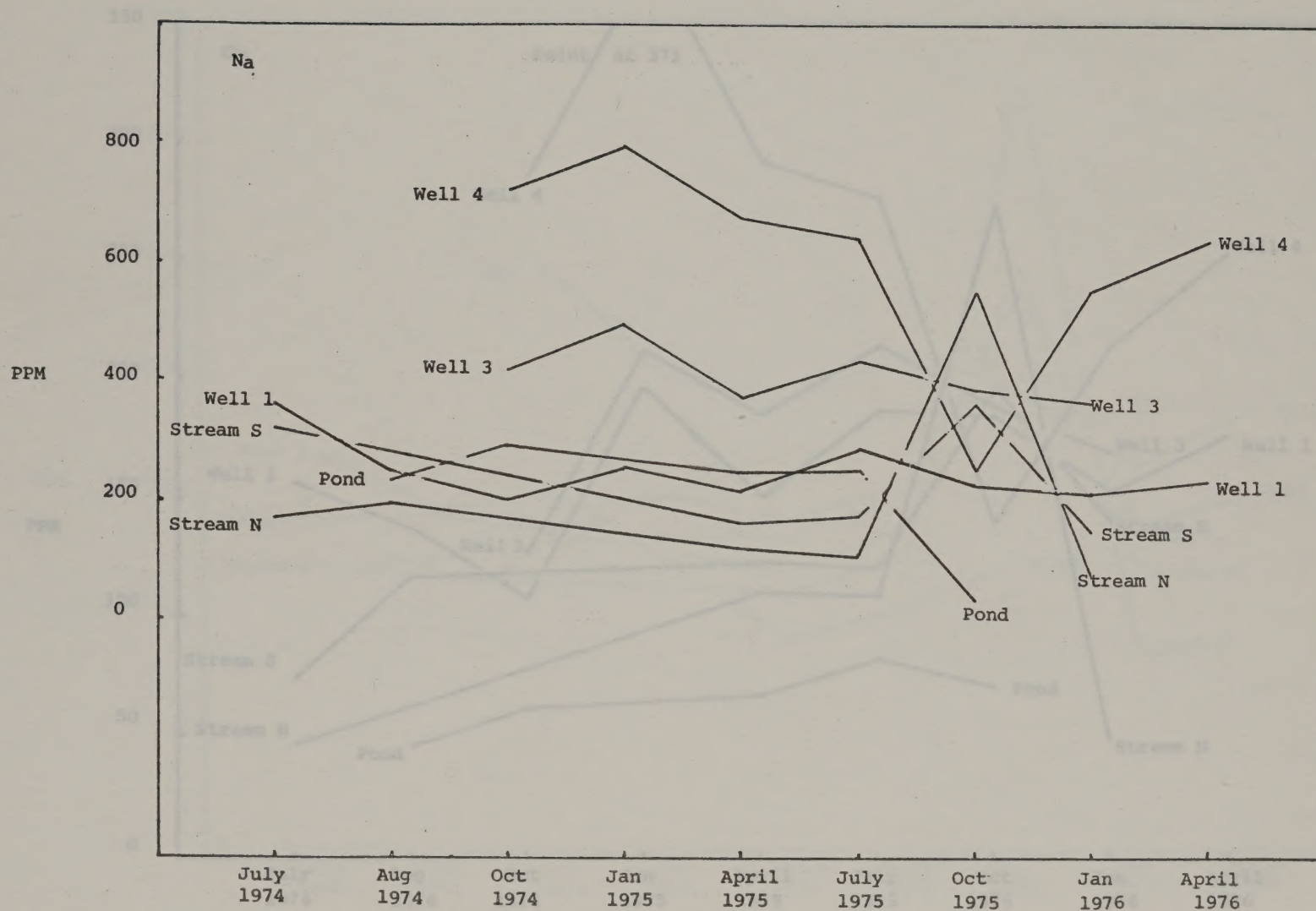
VARIOUS STREAM SAMPLING DATA  
STATIONS

Parameter	B	C	D	E	F
Sodium	484	214	302	128	122
Potassium	10.2	7.1	23.2	4.2	3.7
Calcium	88.1	78.2	84.4	78.2	70.2
Magnesium	26.8	29.2	62.7	66.8	62.2
Aluminum	1.6	2.0	3.4	3.2	1.4
Iron	2.6	0.3	1.2	0.4	0.2
Zinc	0.02	0.06	0.06	0.06	0.12
Chloride	2	7	22	4	2
Sulfate	628	278	888	422	667
Oil & Grease	17.0	24.4	32.6	27.2	11.4
Alkalinity	724	326	381	326	422
Total Dissolved Solids	1222	1412	1712	1280	1022
Total Suspended Solids	2	2	22	2	2
Cadmium	<0.002	<0.002	<0.002	<0.002	<0.002
Copper	0.02	0.04	0.02	0.02	0.02
Lead	<0.1	<0.1	<0.1	<0.1	<0.1
Mercury	0.002	0.002	0.002	0.004	0.002
Fluoride	2.7	0.6	2.7	0.8	1.0
Cyanide	<0.001	<0.001	<0.001	<0.001	<0.001
Sulfide	<0.02	<0.02	<0.02	<0.02	<0.02
Phosphate (as P)	<0.02	0.02	0.02	<0.02	<0.02
Silica (as SiO <sub>2</sub> )	12.0	10.7	11.1	11.7	14.1
Nitrogen, Kjeldahl	1.2	0.8	<0.2	1.2	<0.2
Oxygen, Chemical Demand	41.2	32.1	26.4	22.2	12.8
Phenols	0.002	<0.001	0.002	0.002	0.004
pH	8.20	8.16	8.12	8.01	7.88
Boron	<0.1	<0.1	<0.1	<0.1	<0.1
Arsenic	0.004	0.002	0.002	0.002	0.001
Molybdenum	2.0	<0.2	<0.2	<0.2	<0.2

NOTE: All data are in ppm except pH

I.E. - Insufficient sample remaining to perform determination.

FIGURE IV-B-1  
SODIUM





# FIGURE 1A-2-1

SECTION

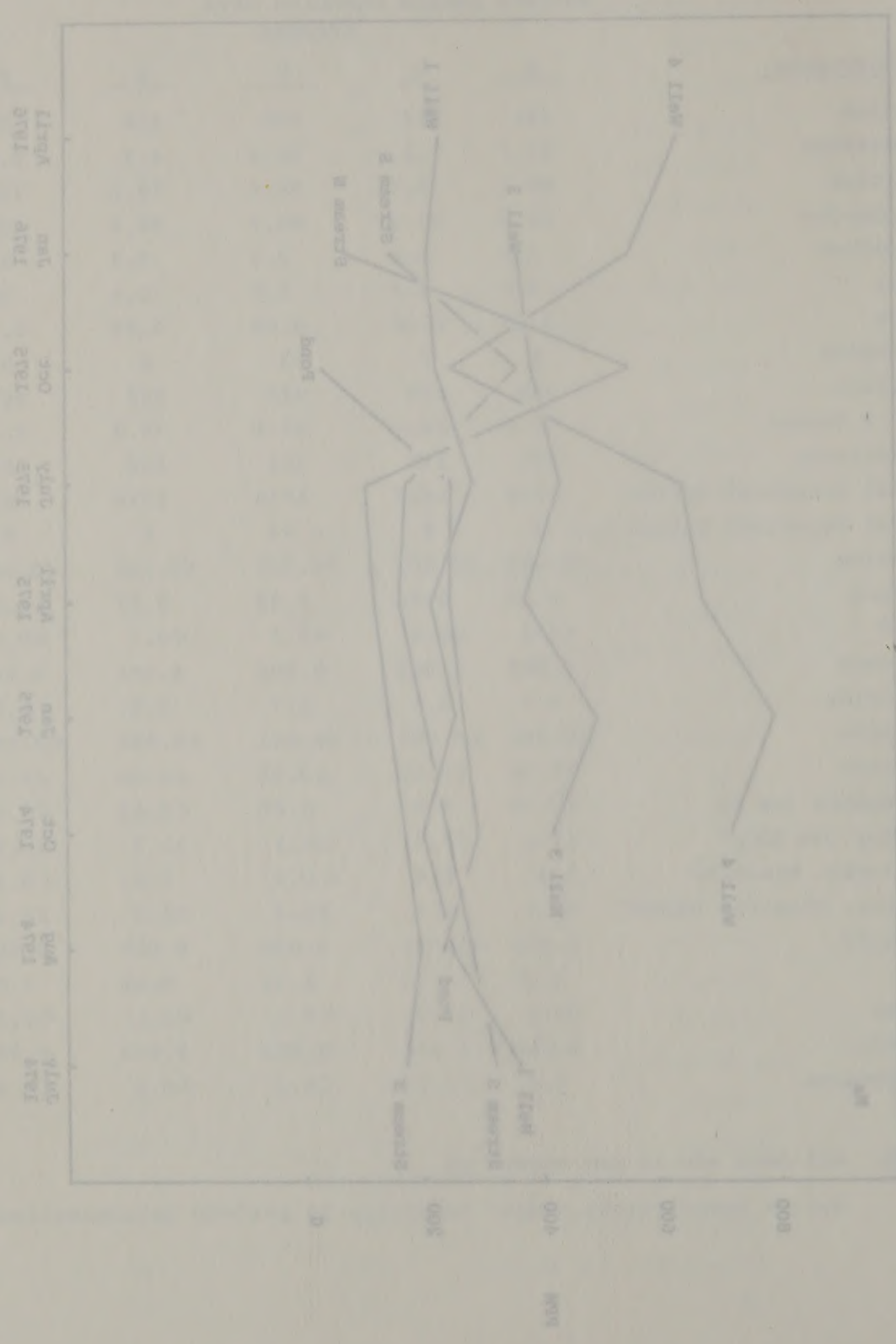


FIGURE IV-B-2  
CALCIUM

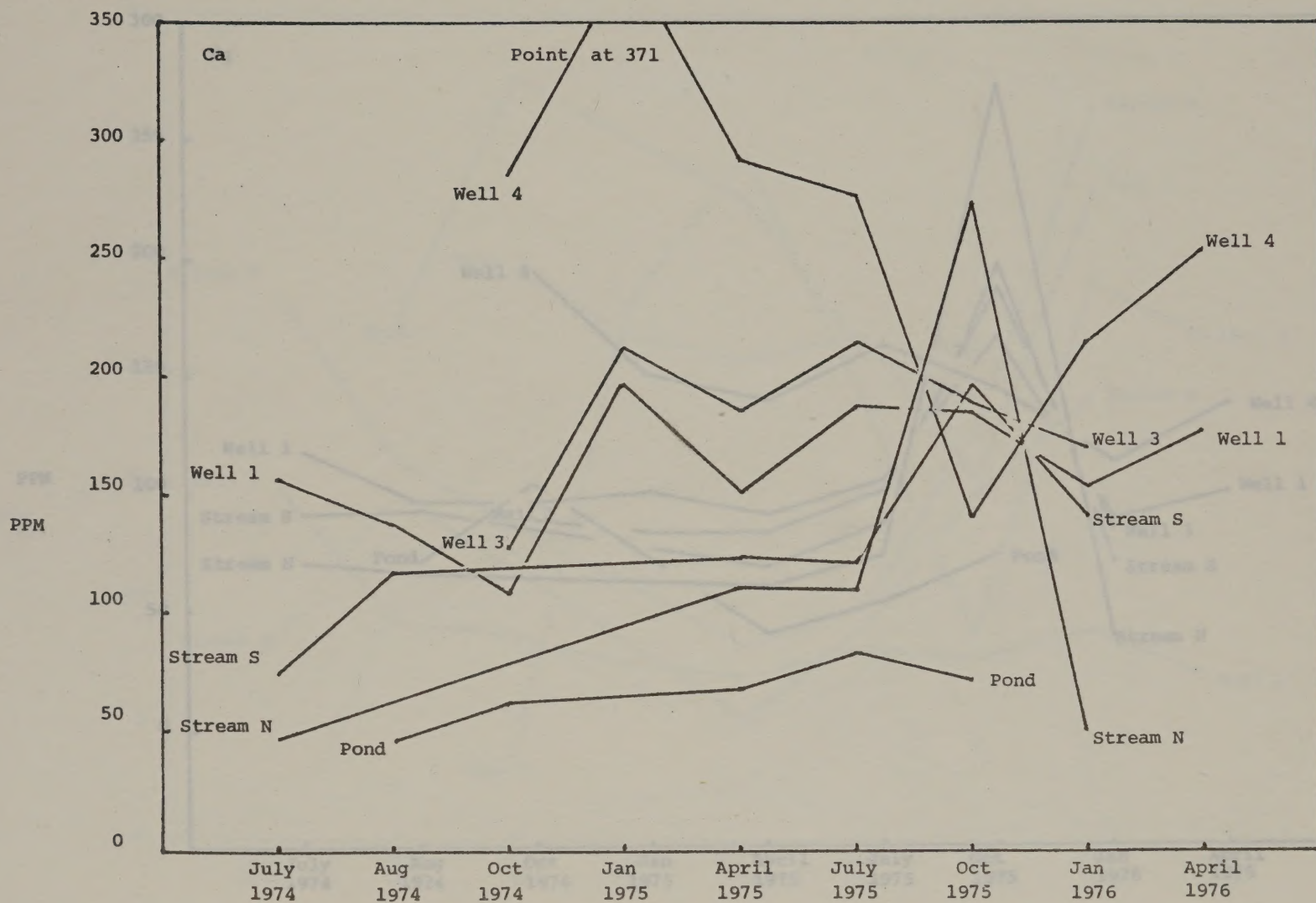




FIGURE 1A-B-3  
CARTON

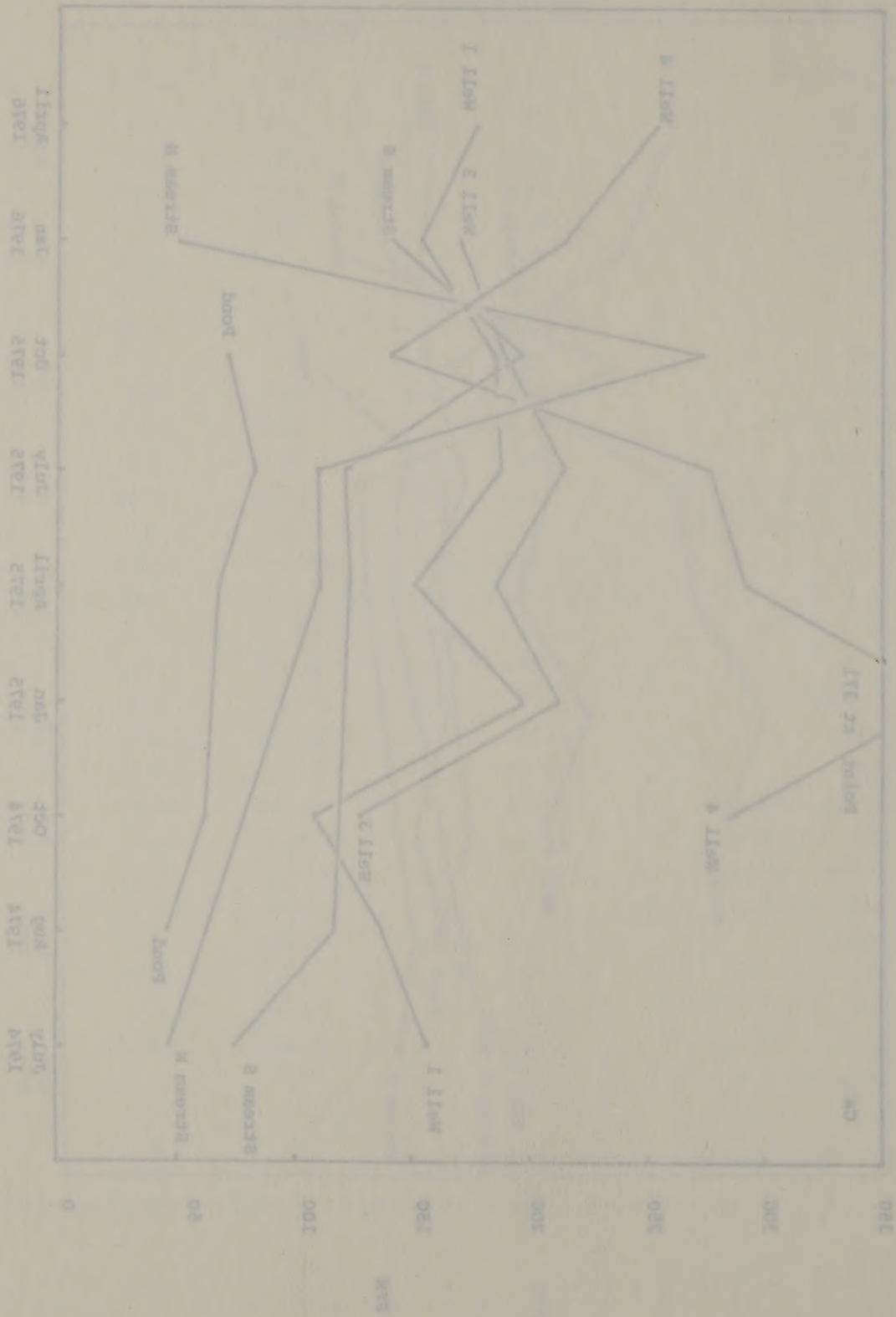


FIGURE IV-B-3  
MAGNESIUM

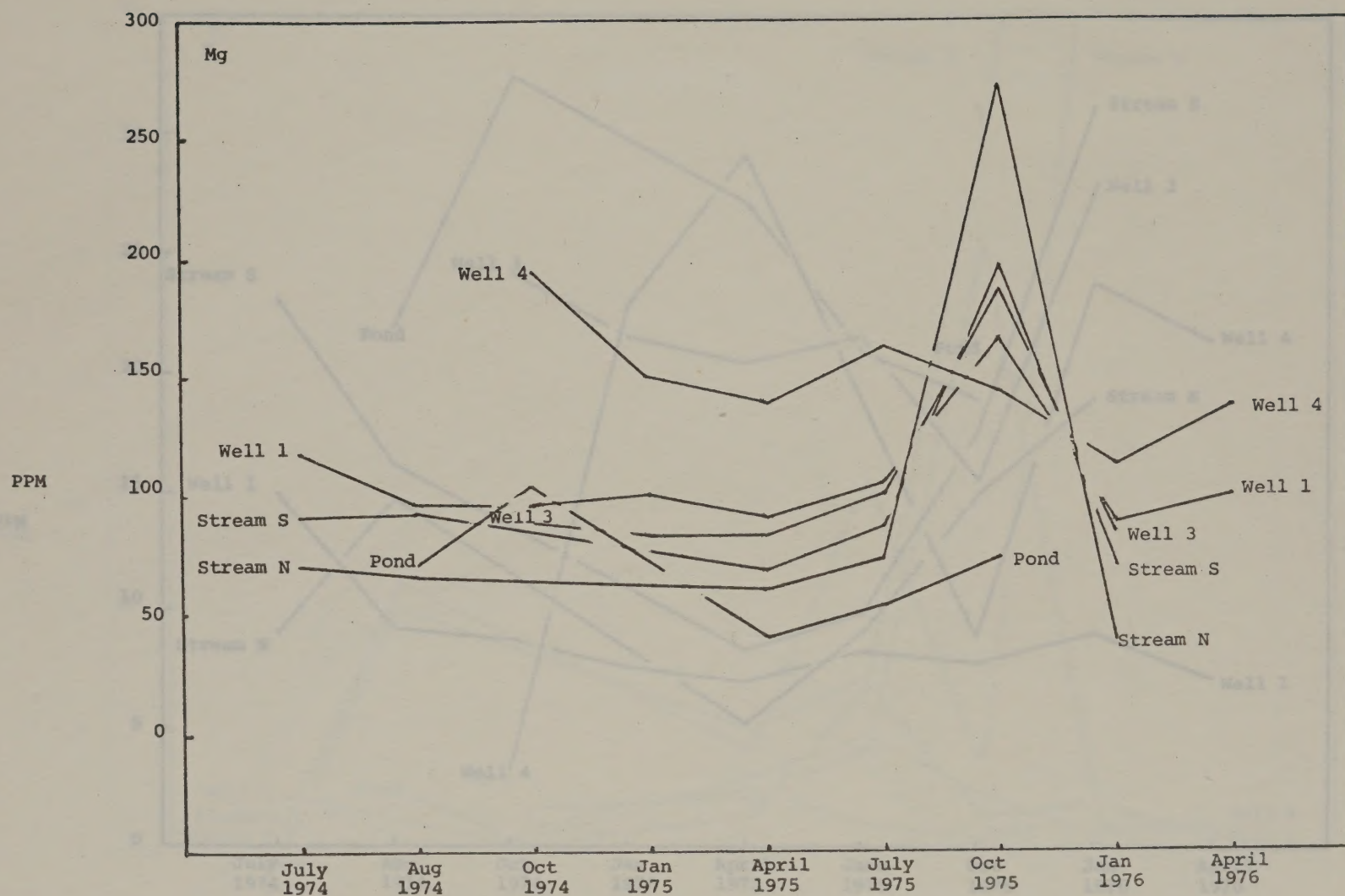




FIGURE IV-2-1  
WATERFALL

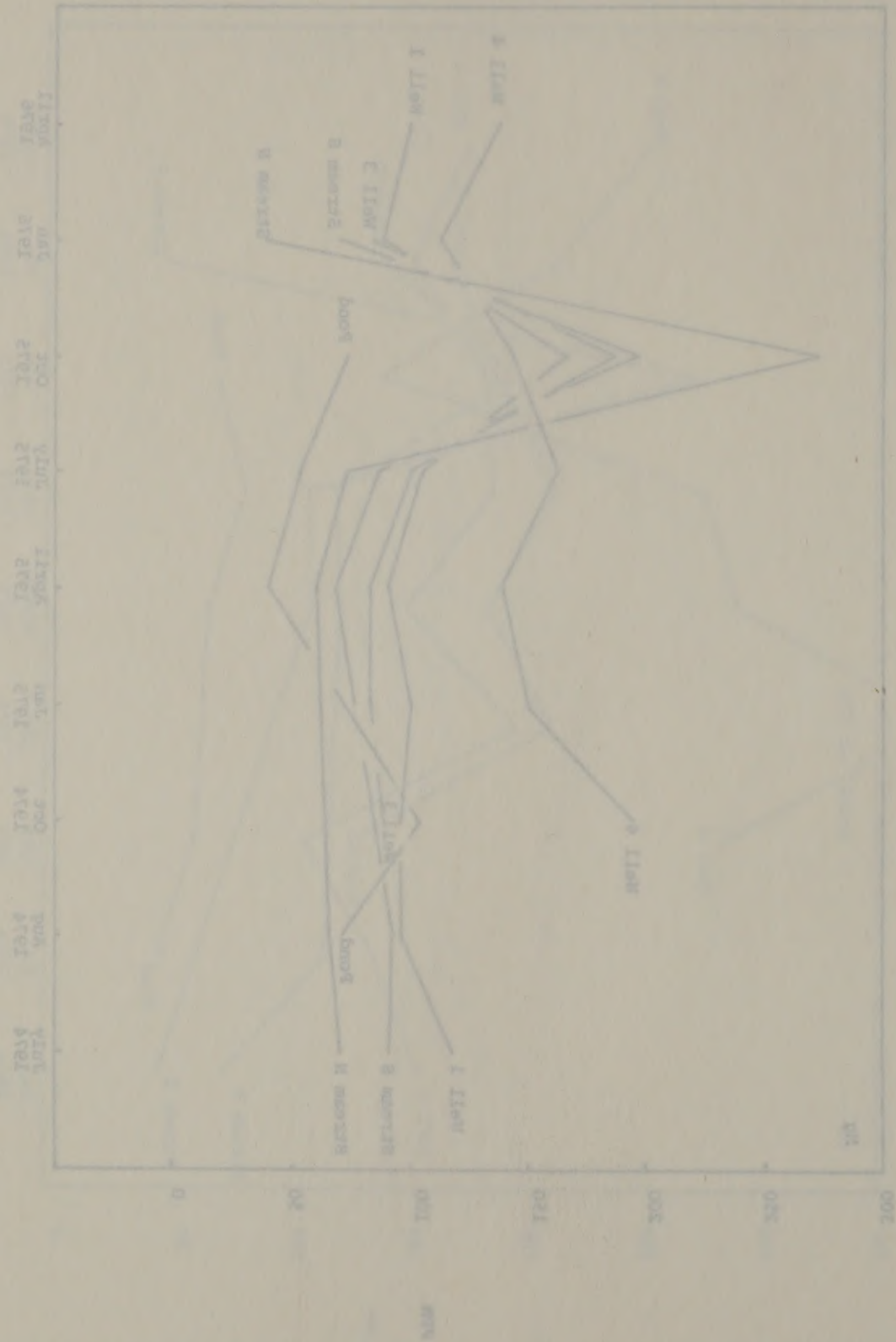


FIGURE IV-B-4  
POTASSIUM

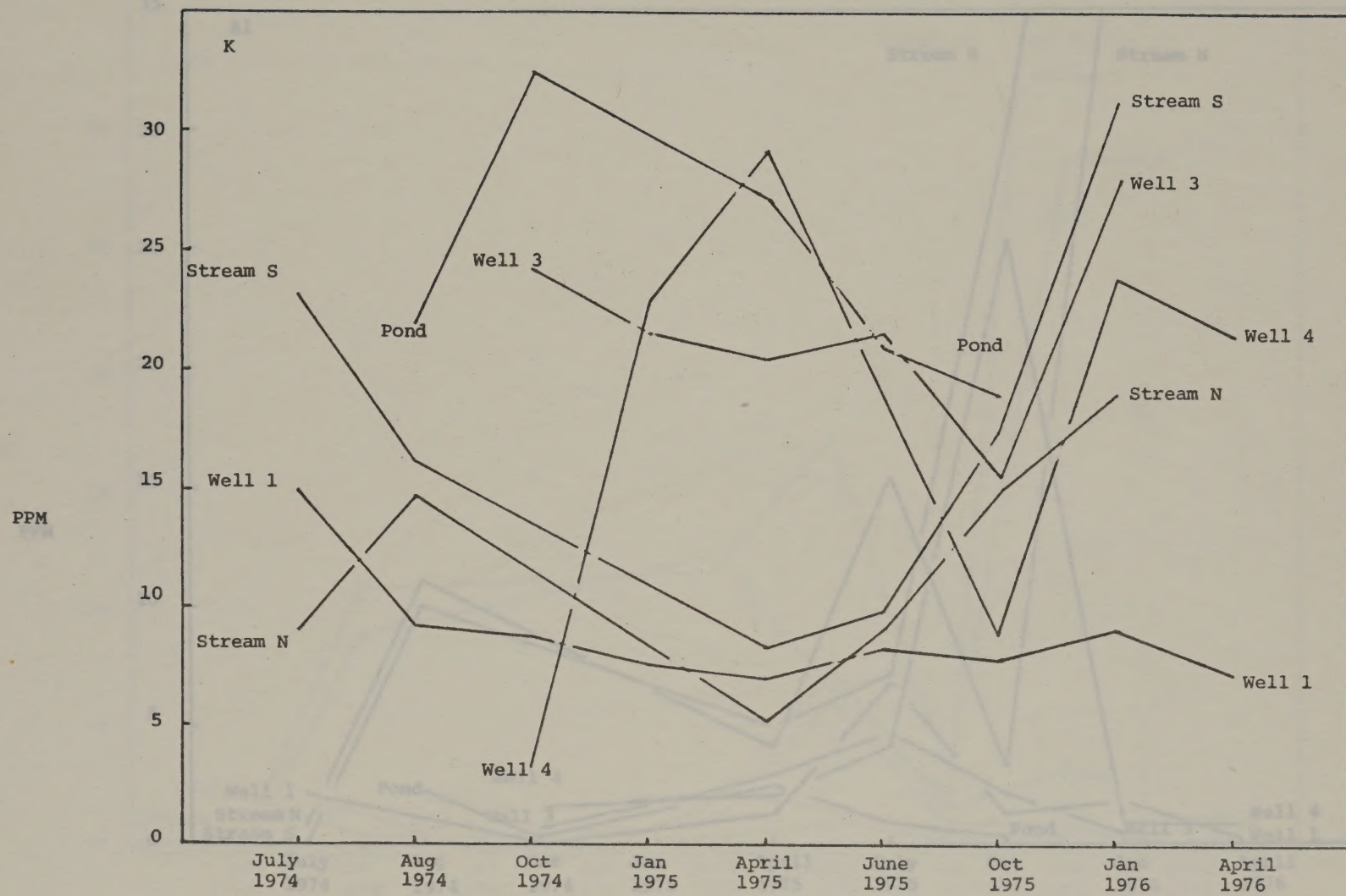




FIGURE IV-2-1

BOATWATER

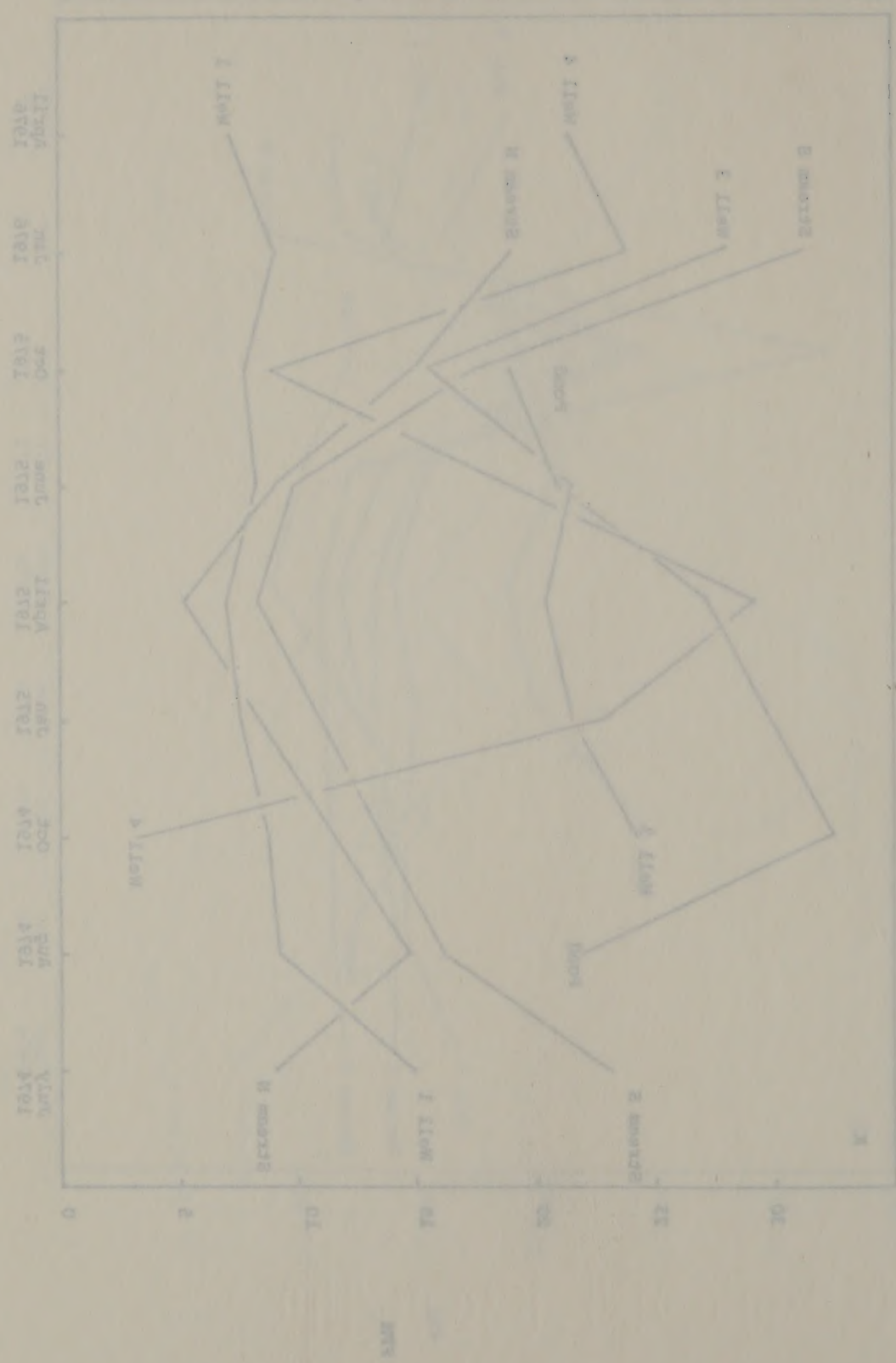
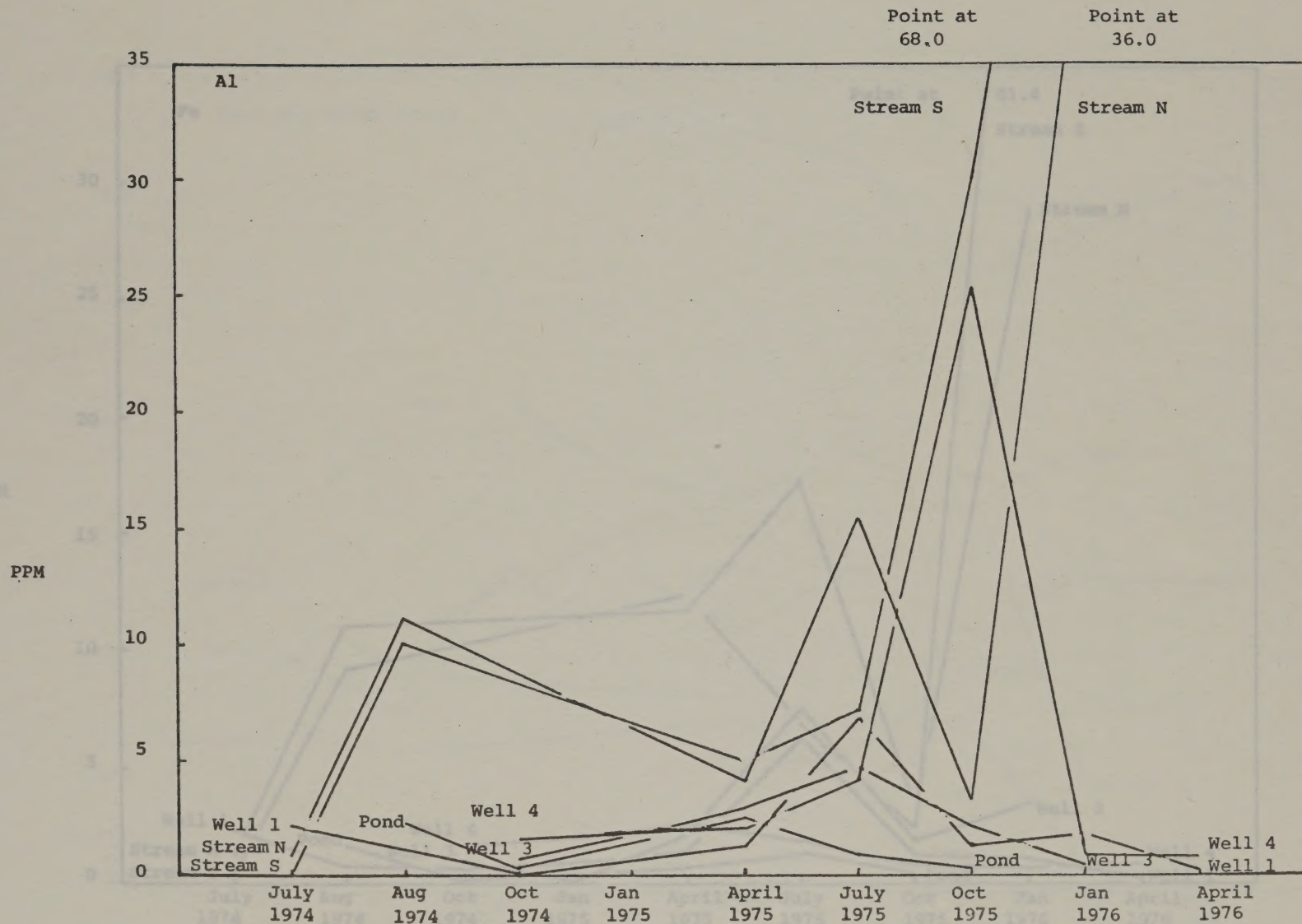


FIGURE IV-B-5  
ALUMINUM





2-4-71 11:11

ALABAMA

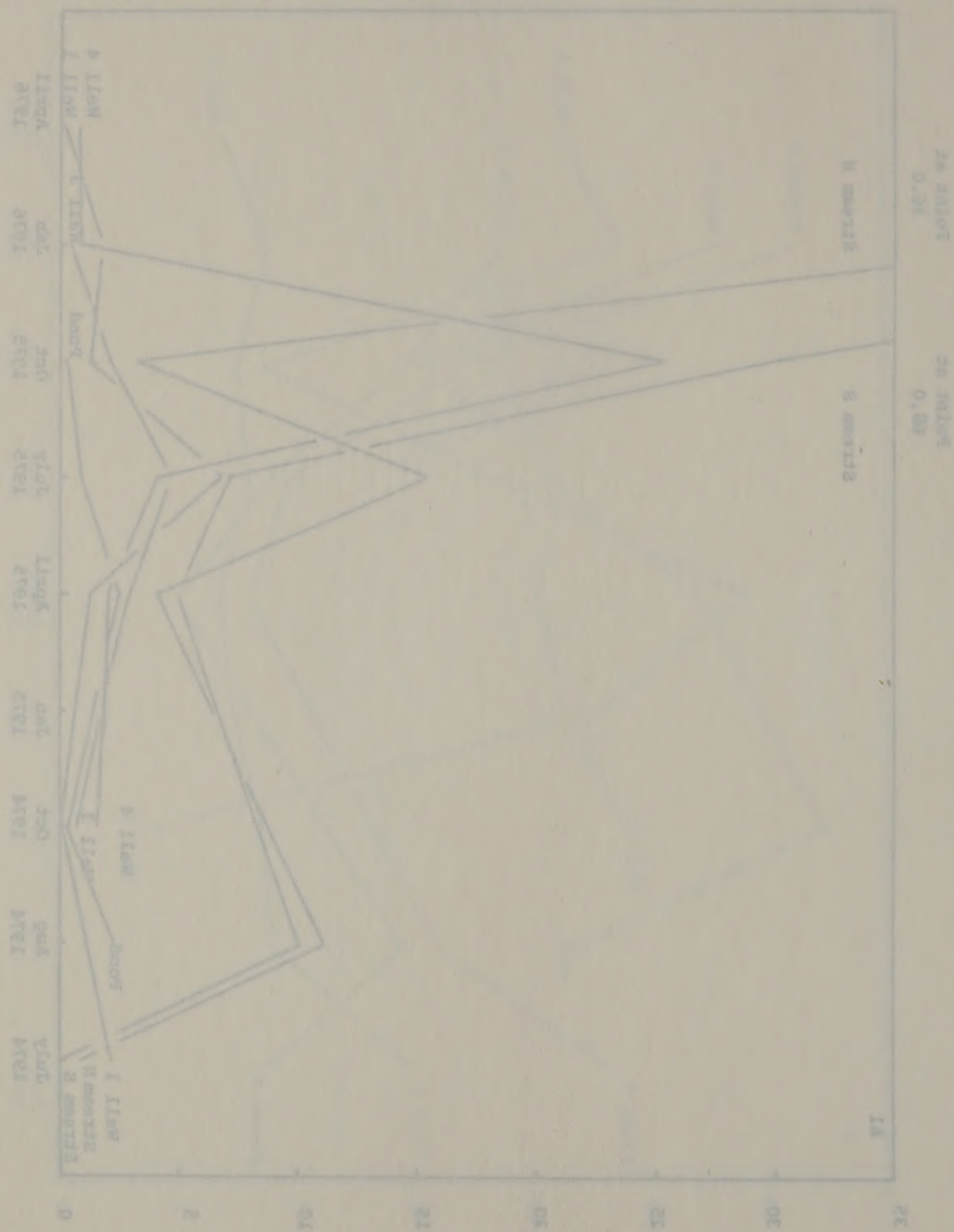


FIGURE IV-B-6

IRON

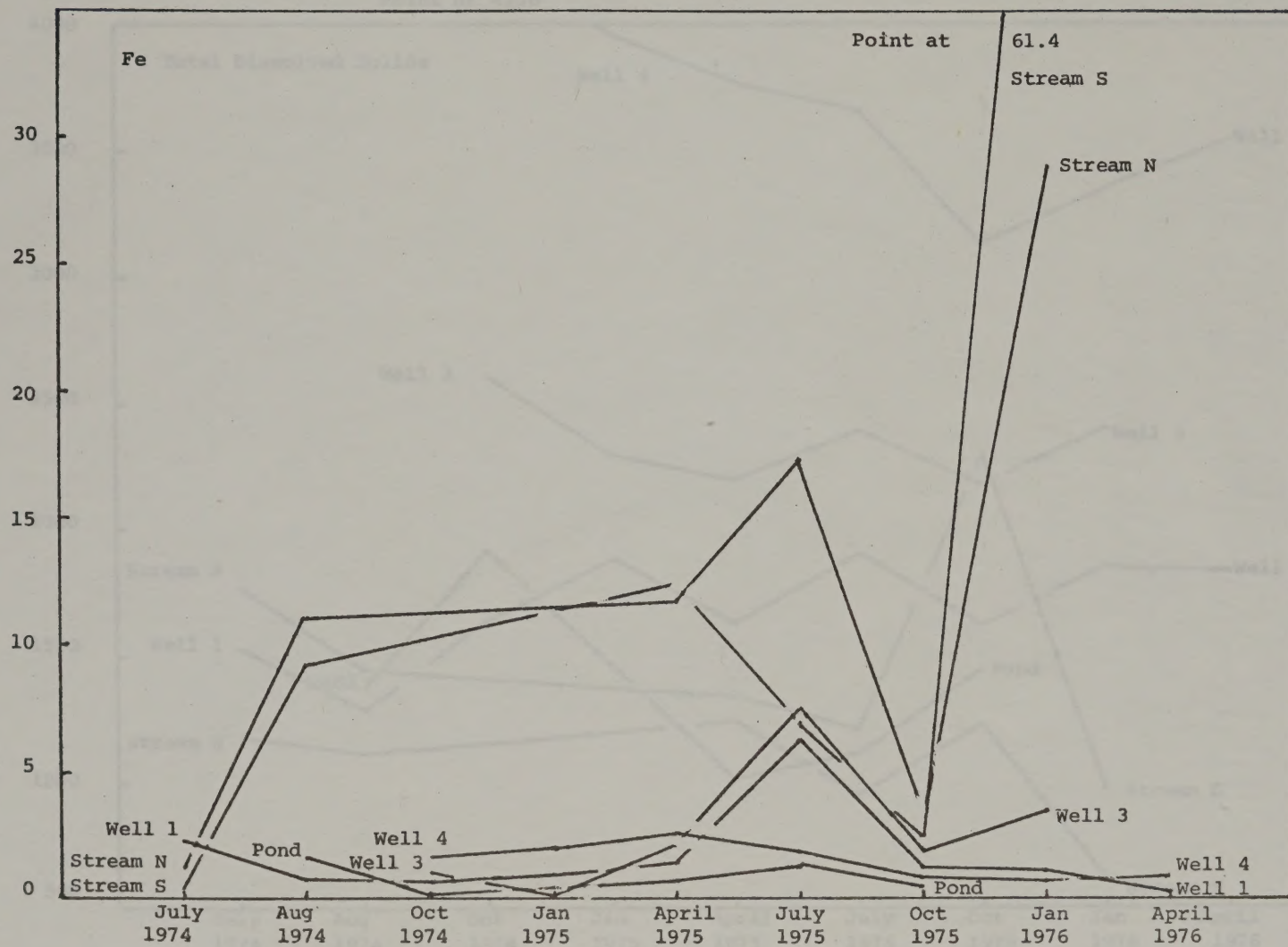




FIGURE 17-B-2

WATER

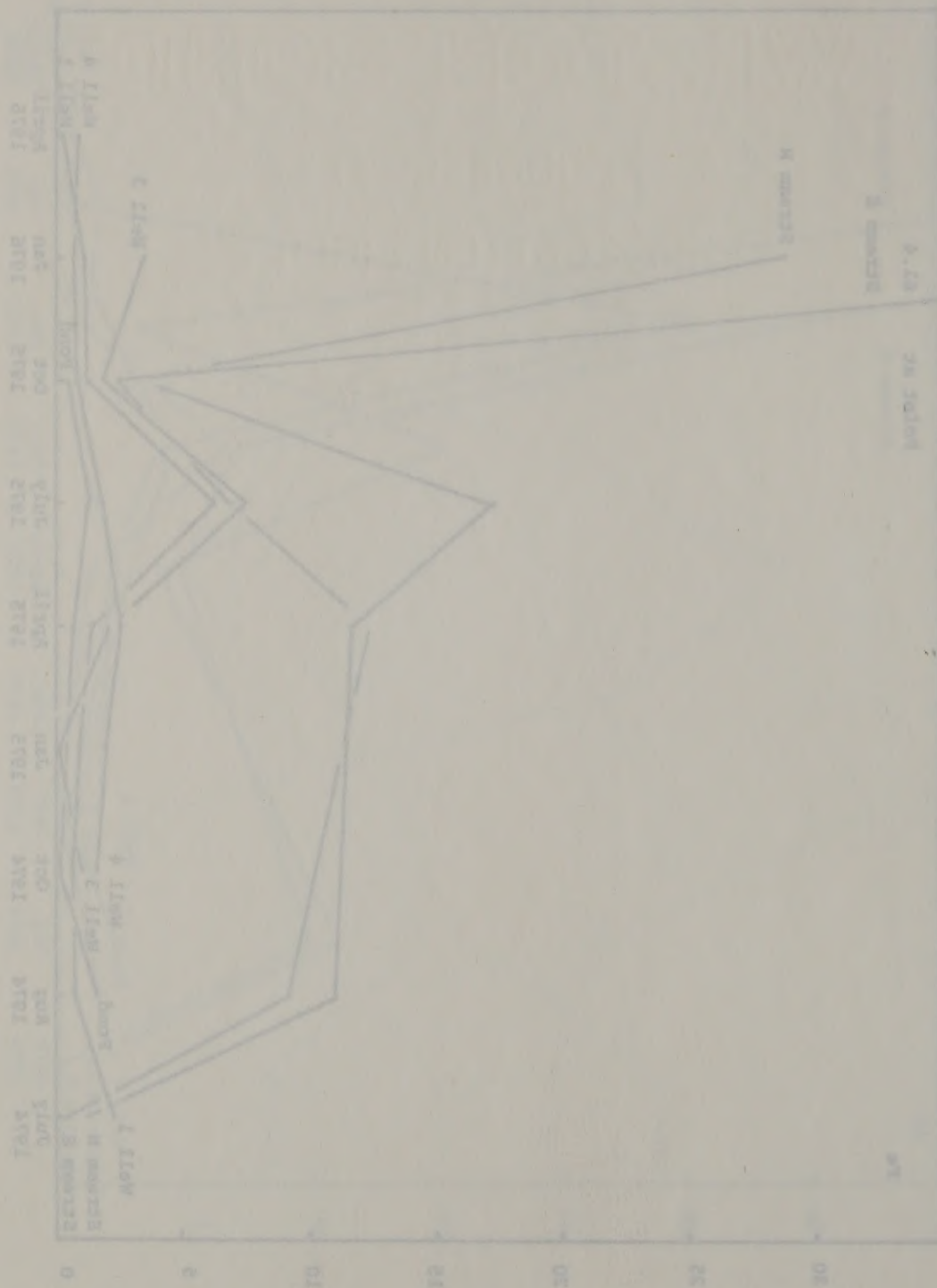
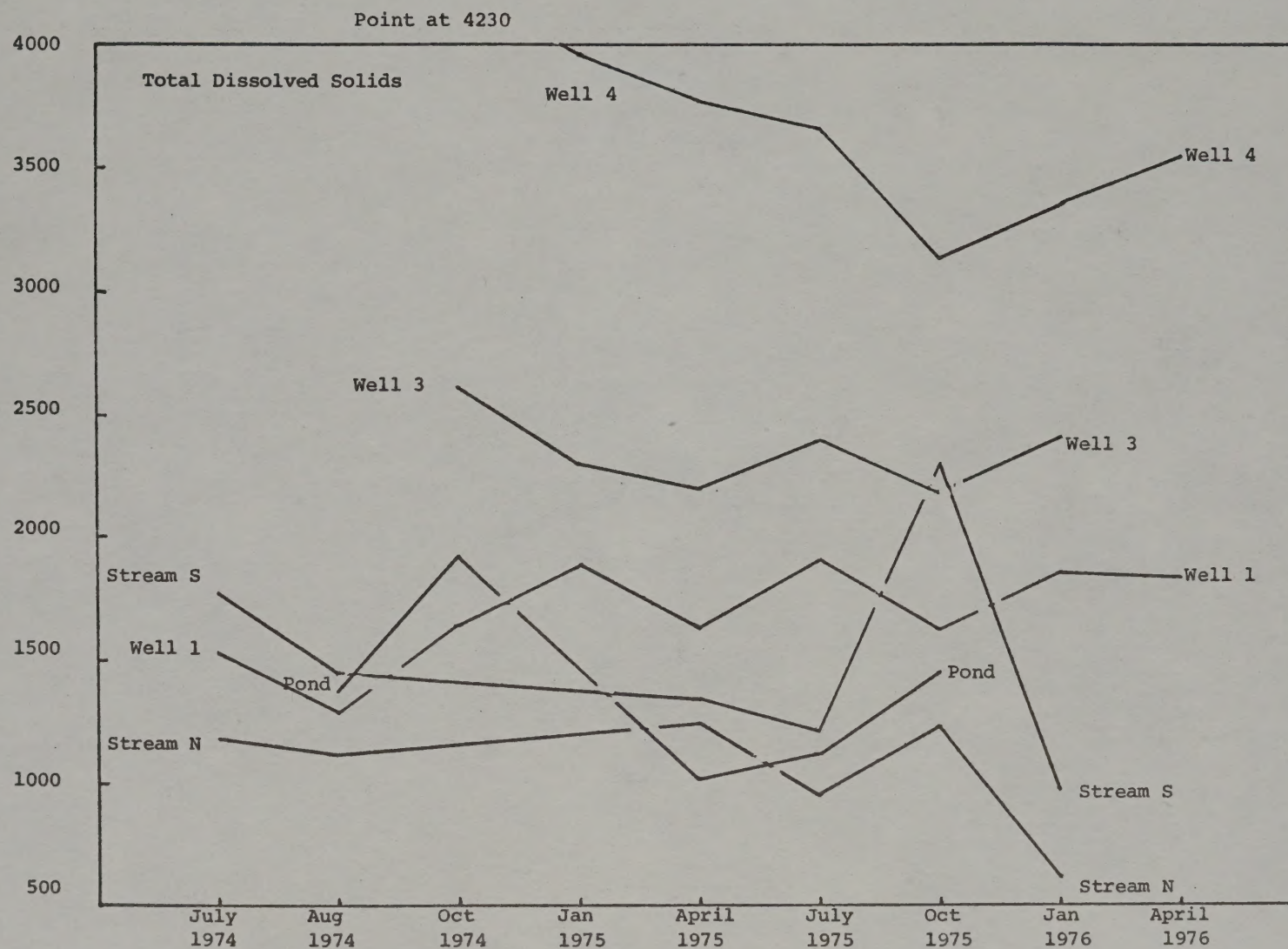


FIGURE IV-B-7  
TOTAL DISSOLVED SOLIDS





25 COTTON FIBRE

1453

WESTON BOND

100% COTTON

FIGURE IV-B-8  
TOTAL SUSPENDED SOLIDS

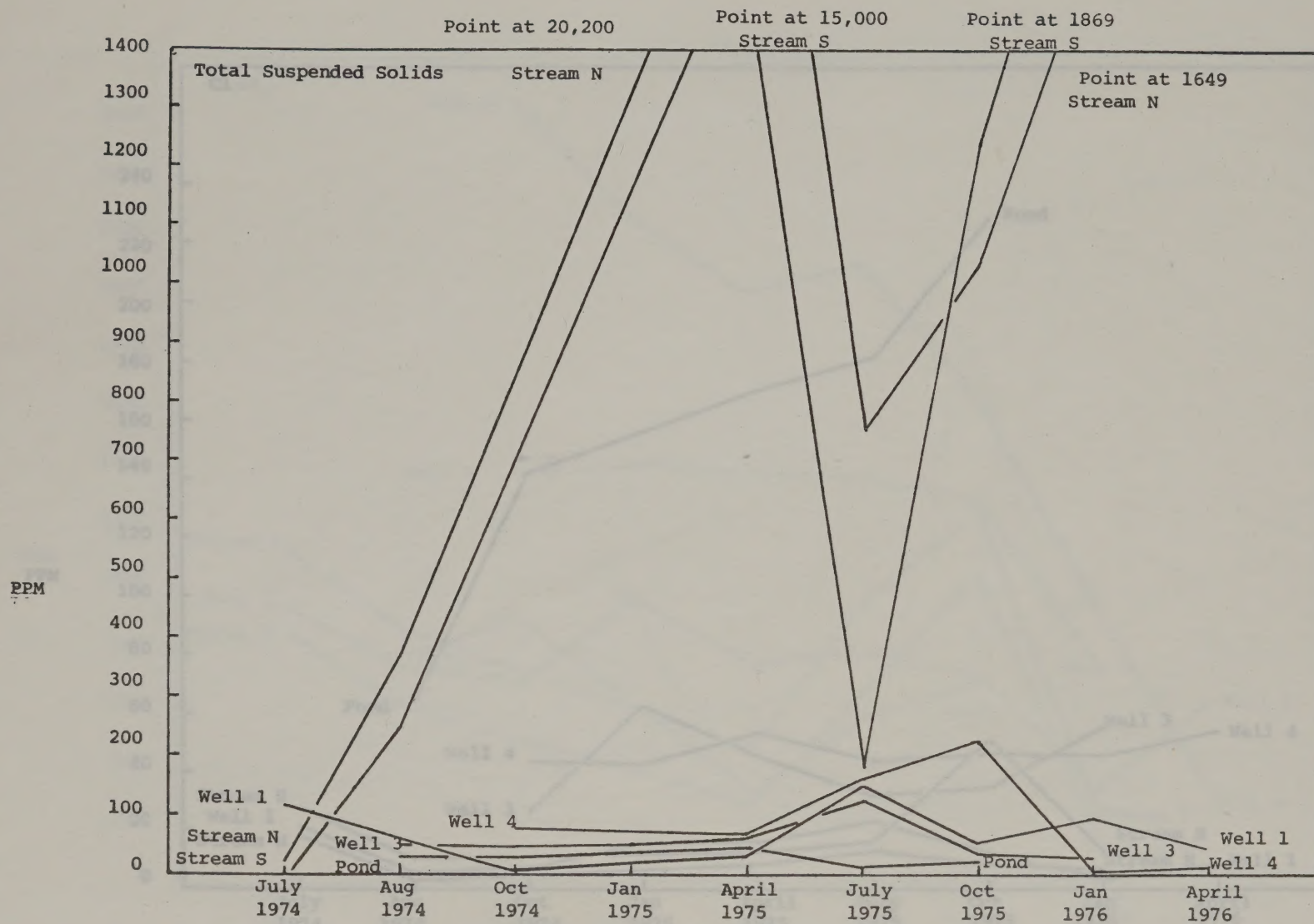




FIGURE 10-2-2  
WATER RESOURCES DIVISION

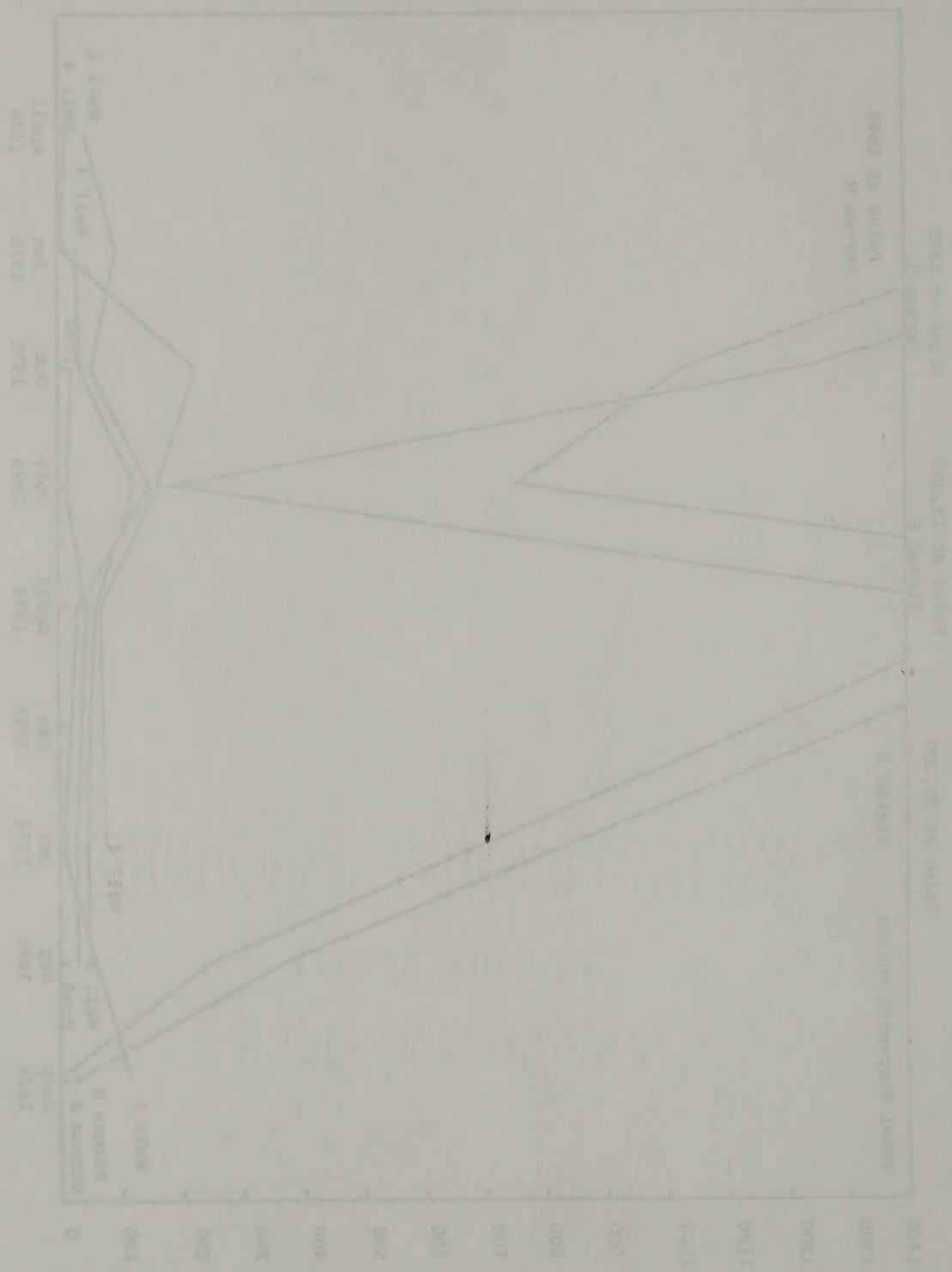


FIGURE IV-B-9  
CHLORIDE

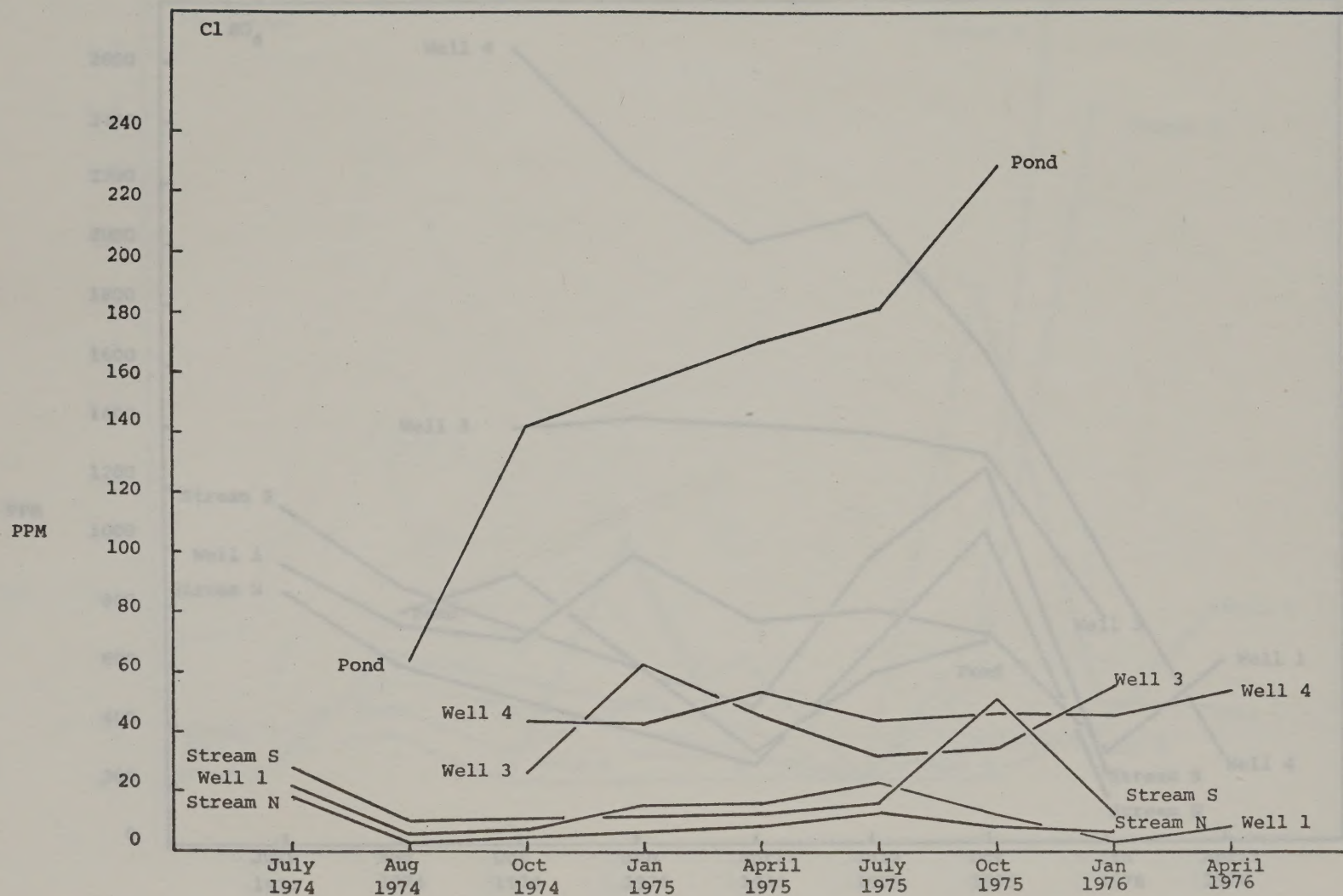






FIGURE IV-B-10  
SULFATE

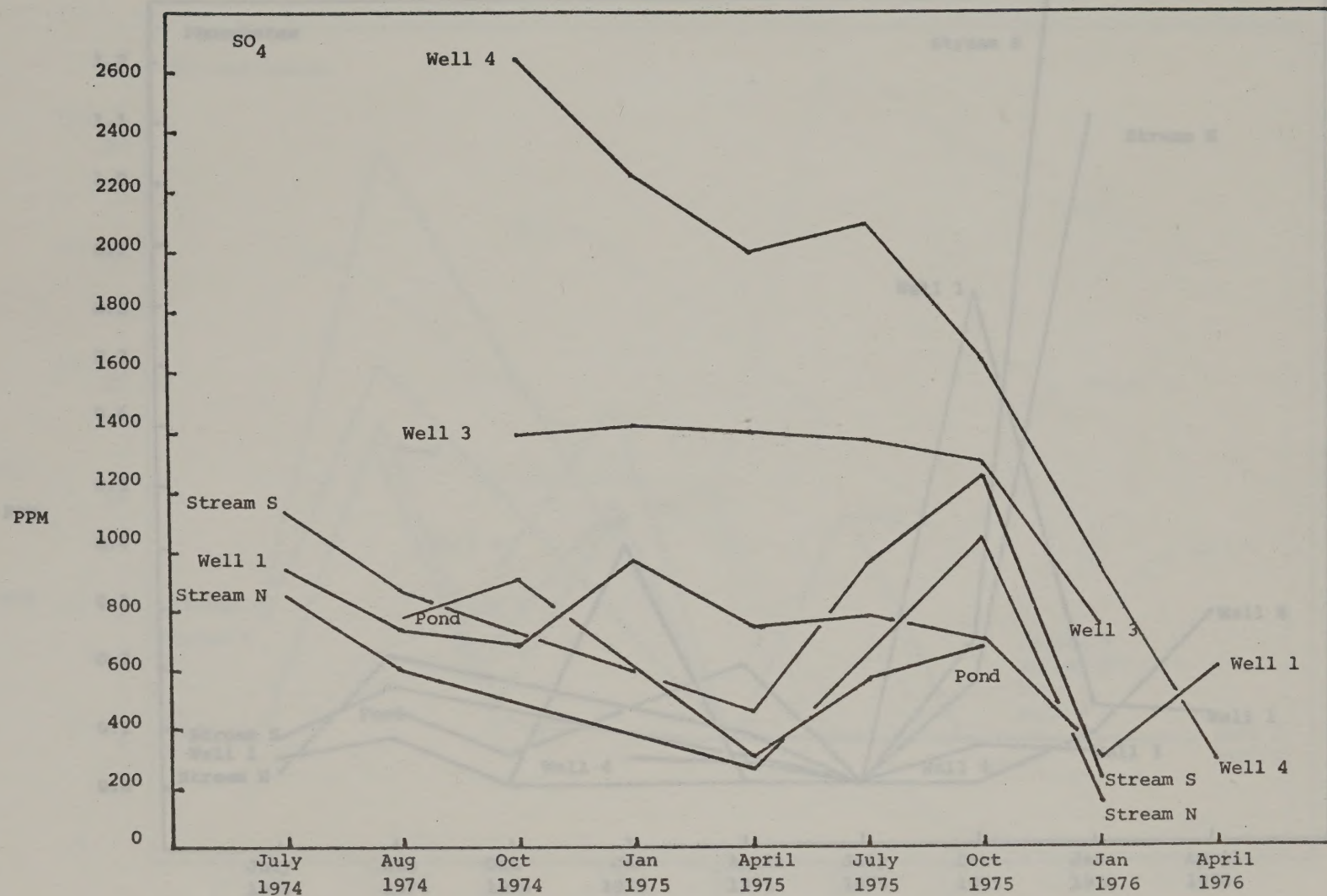






FIGURE IV-B-11

PHOSPHATE

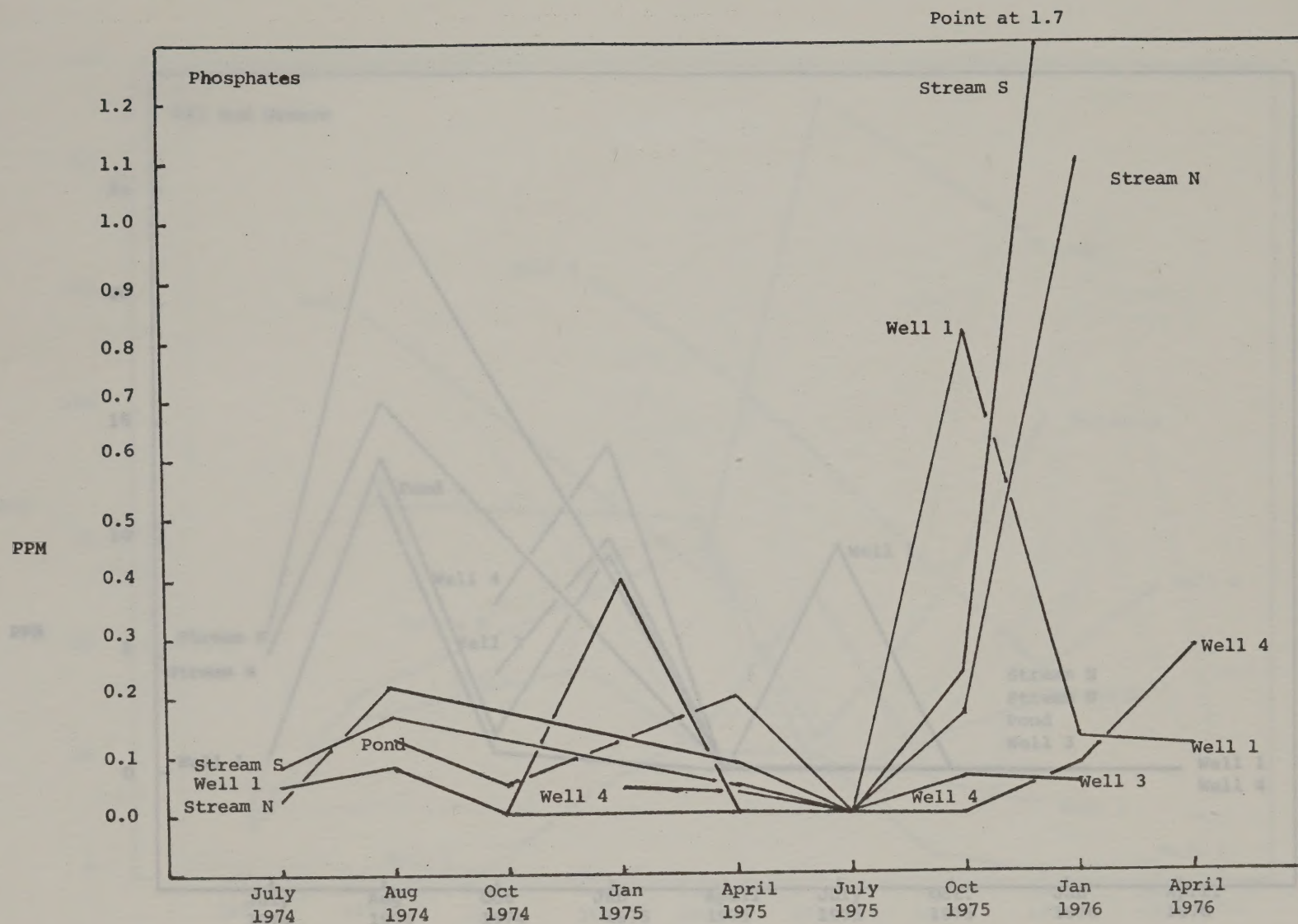




FIGURE 1A-3-71

PROBABILITY

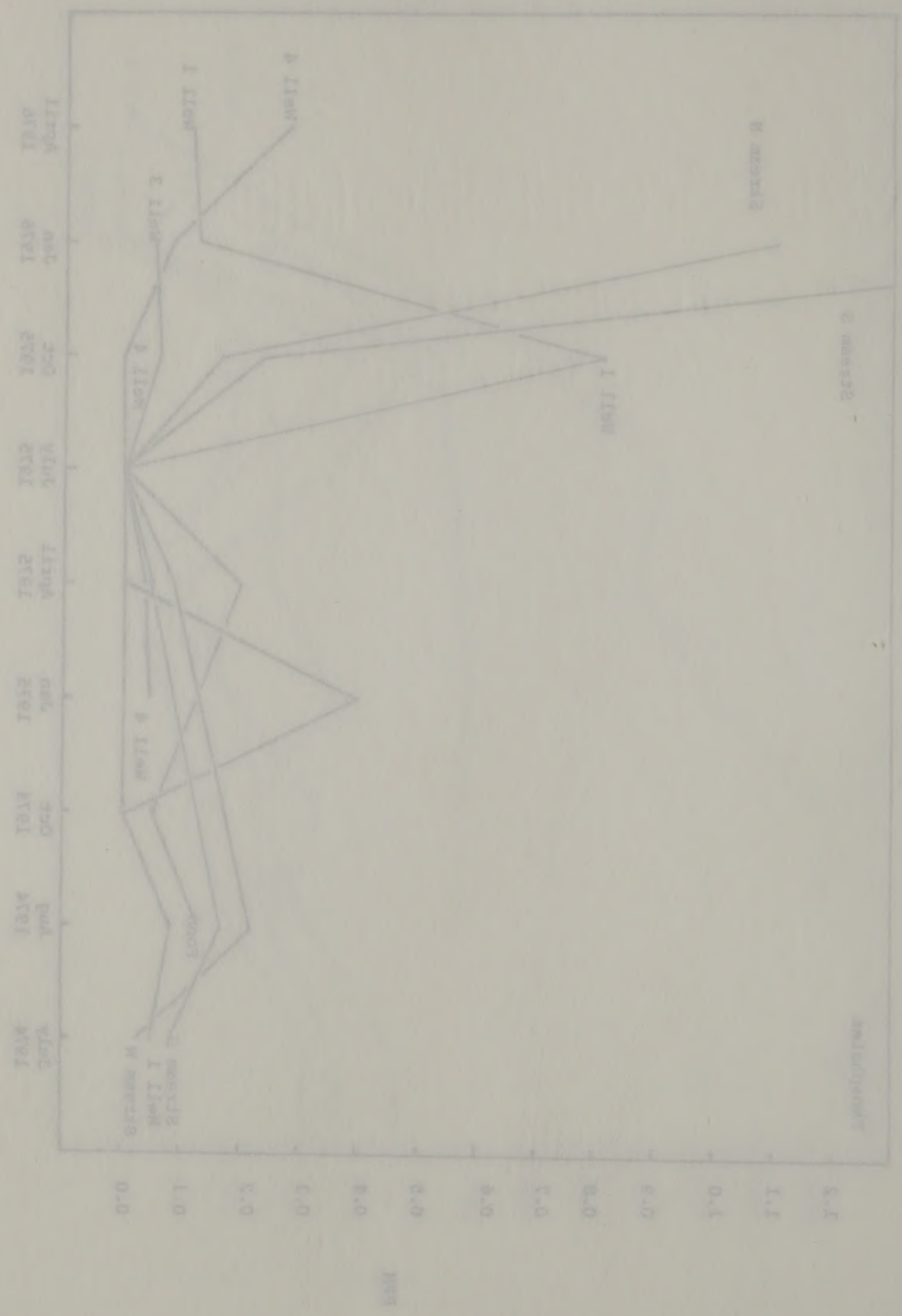


FIGURE IV-B-12  
OIL AND GREASE

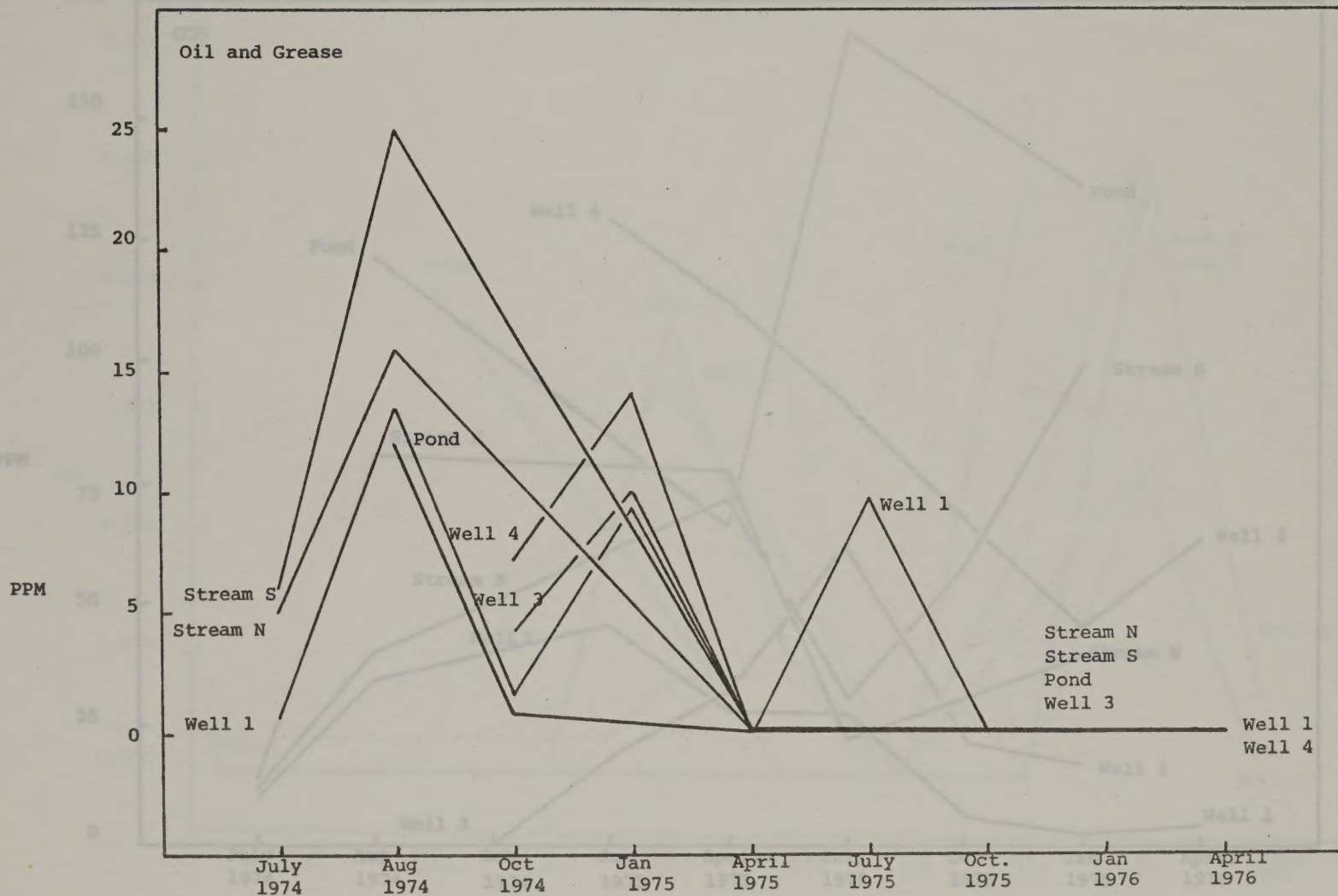
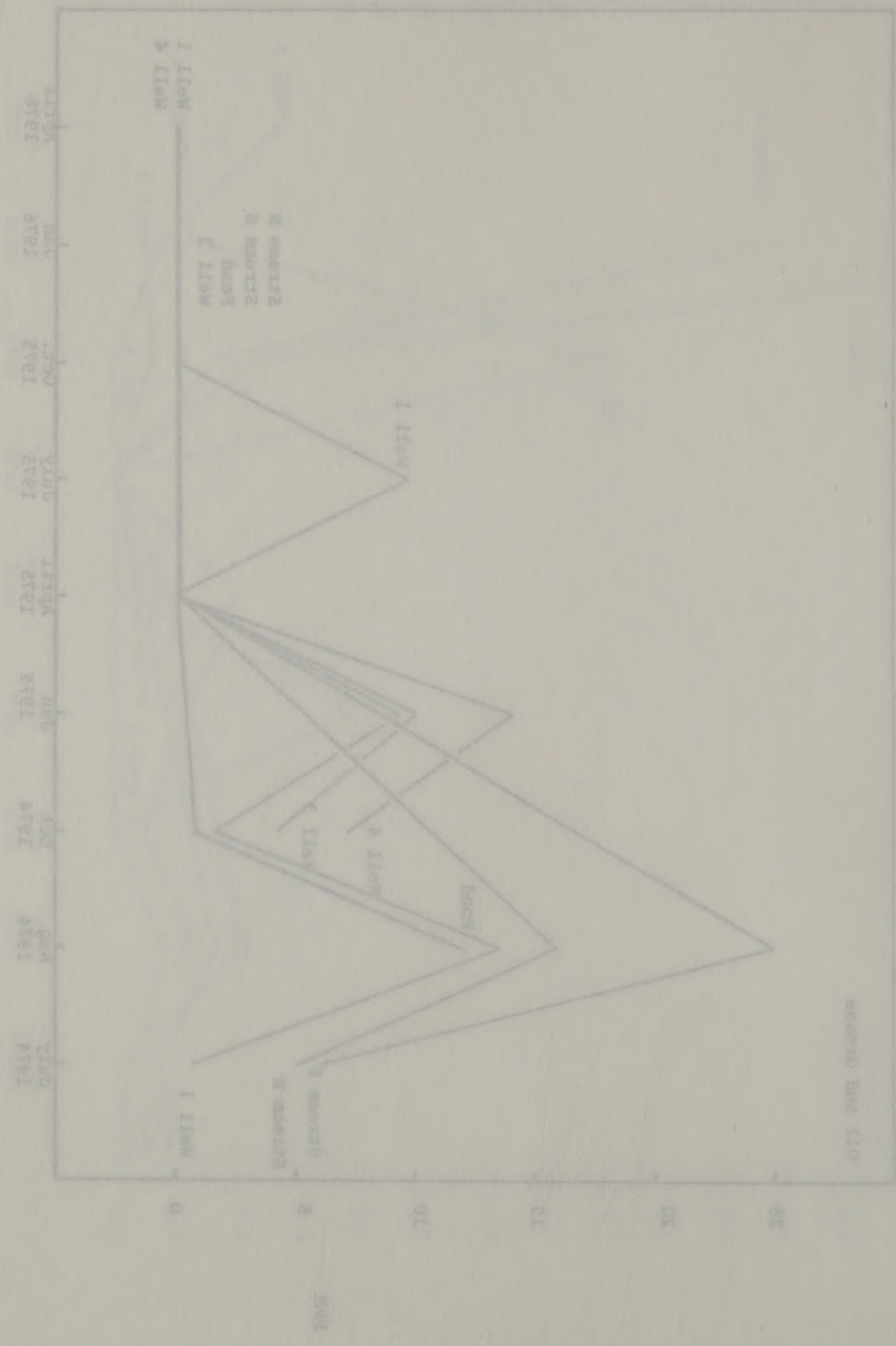




FIGURE 10-11-12  
OIL AND GAS



CHEMICAL OXYGEN DEMAND

FIGURE IV-B-13

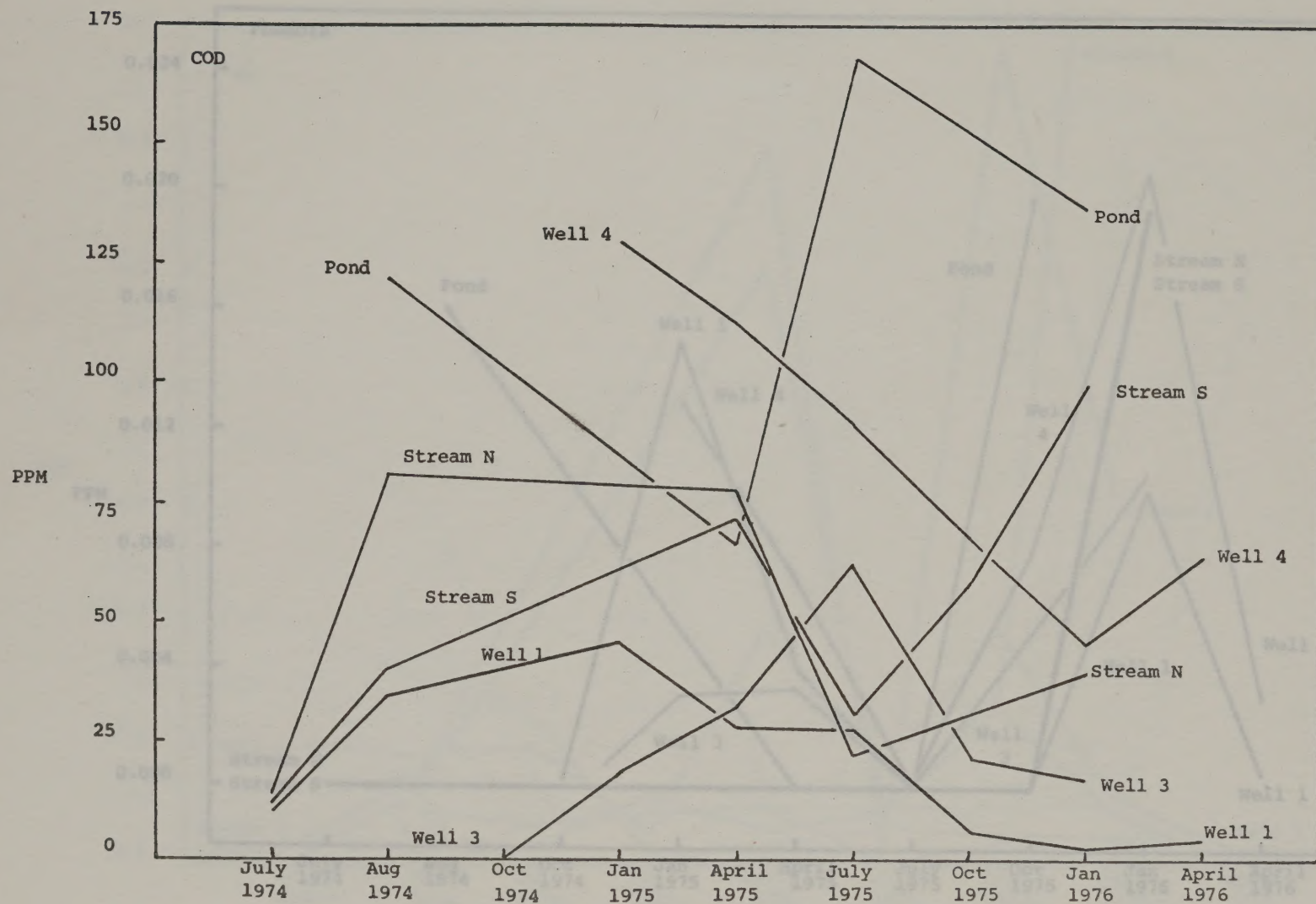






FIGURE IV-B-14  
PHENOLS

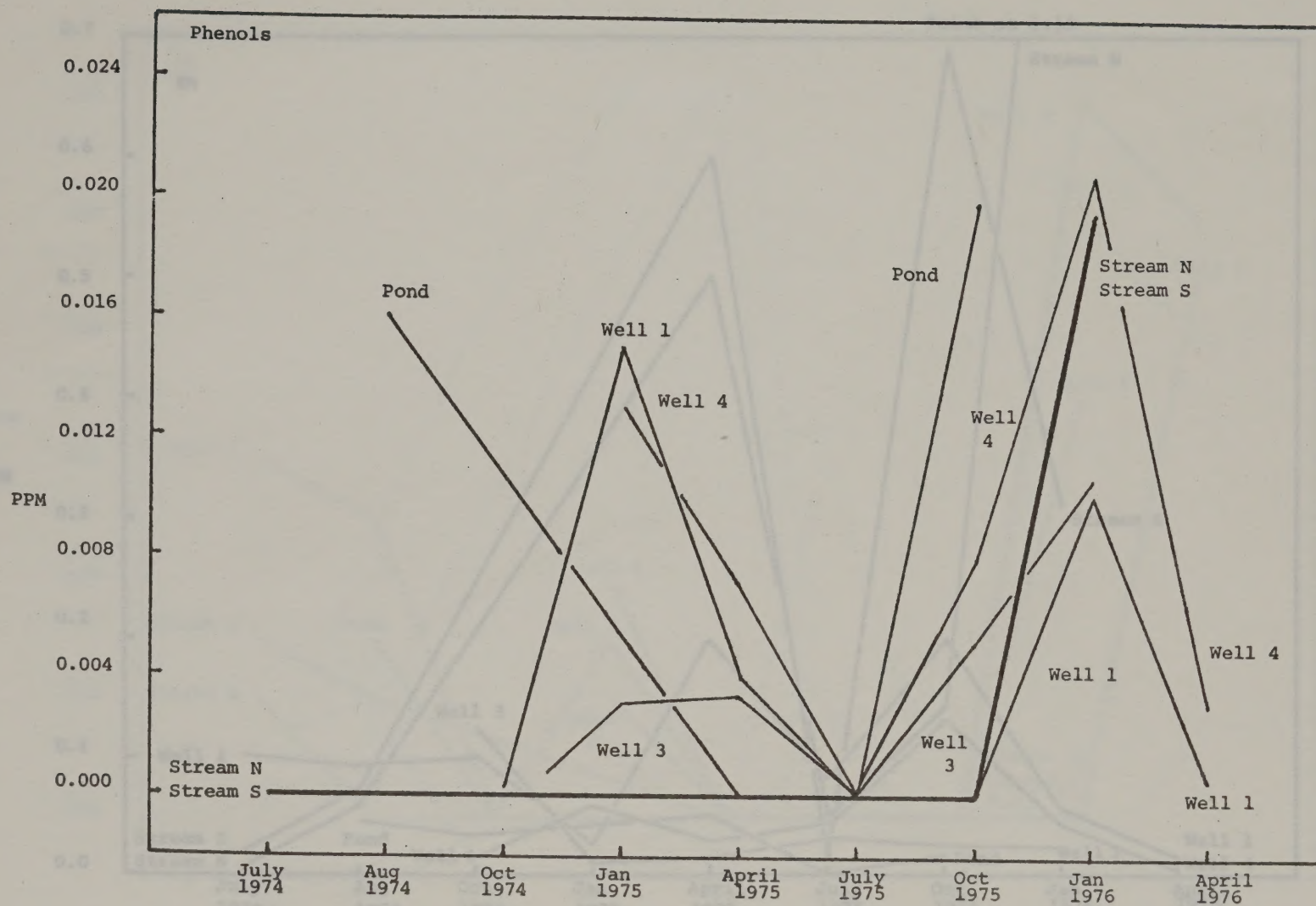




FIGURE IV-B-14

PERCENT

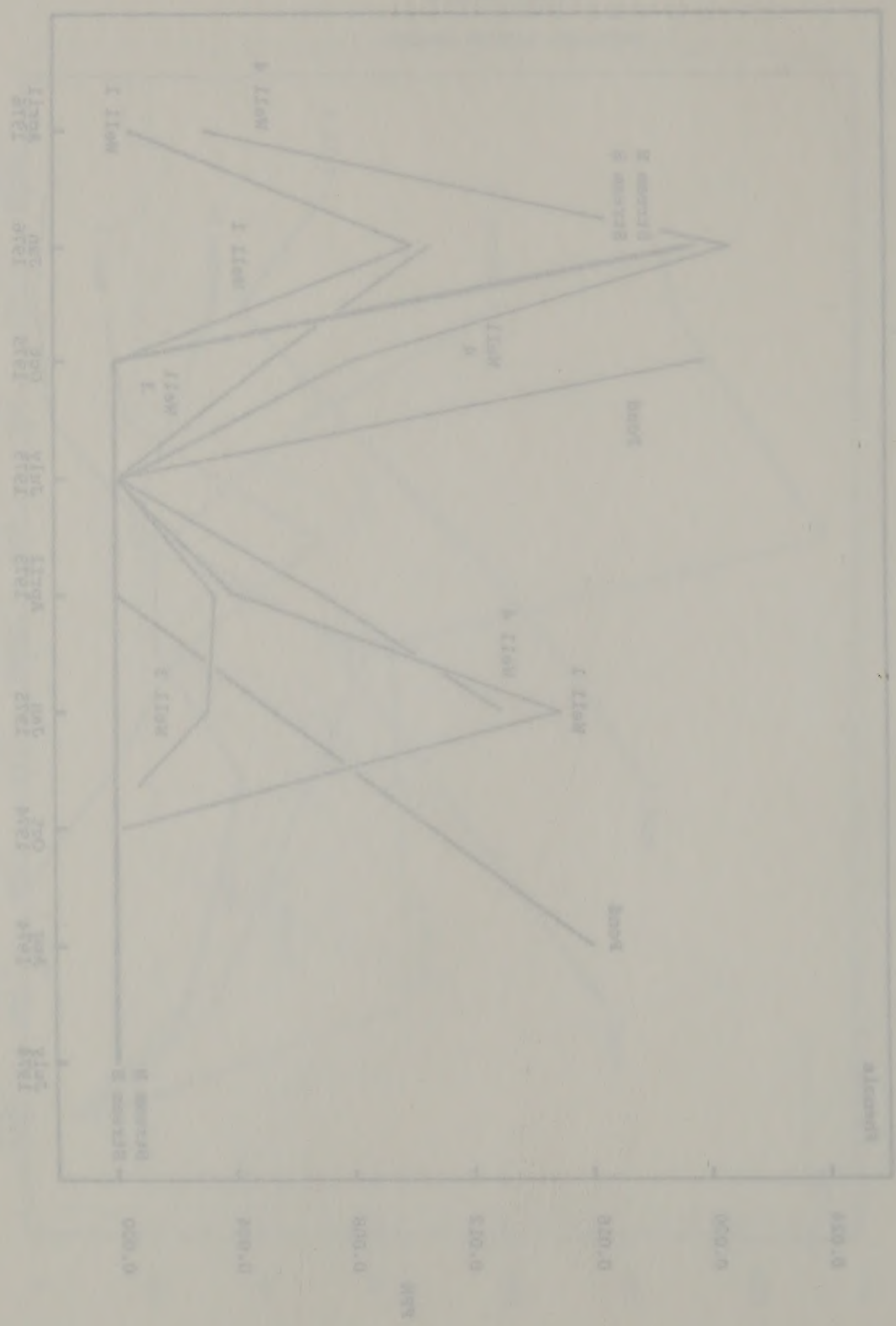


FIGURE IV-B-15  
ZINC

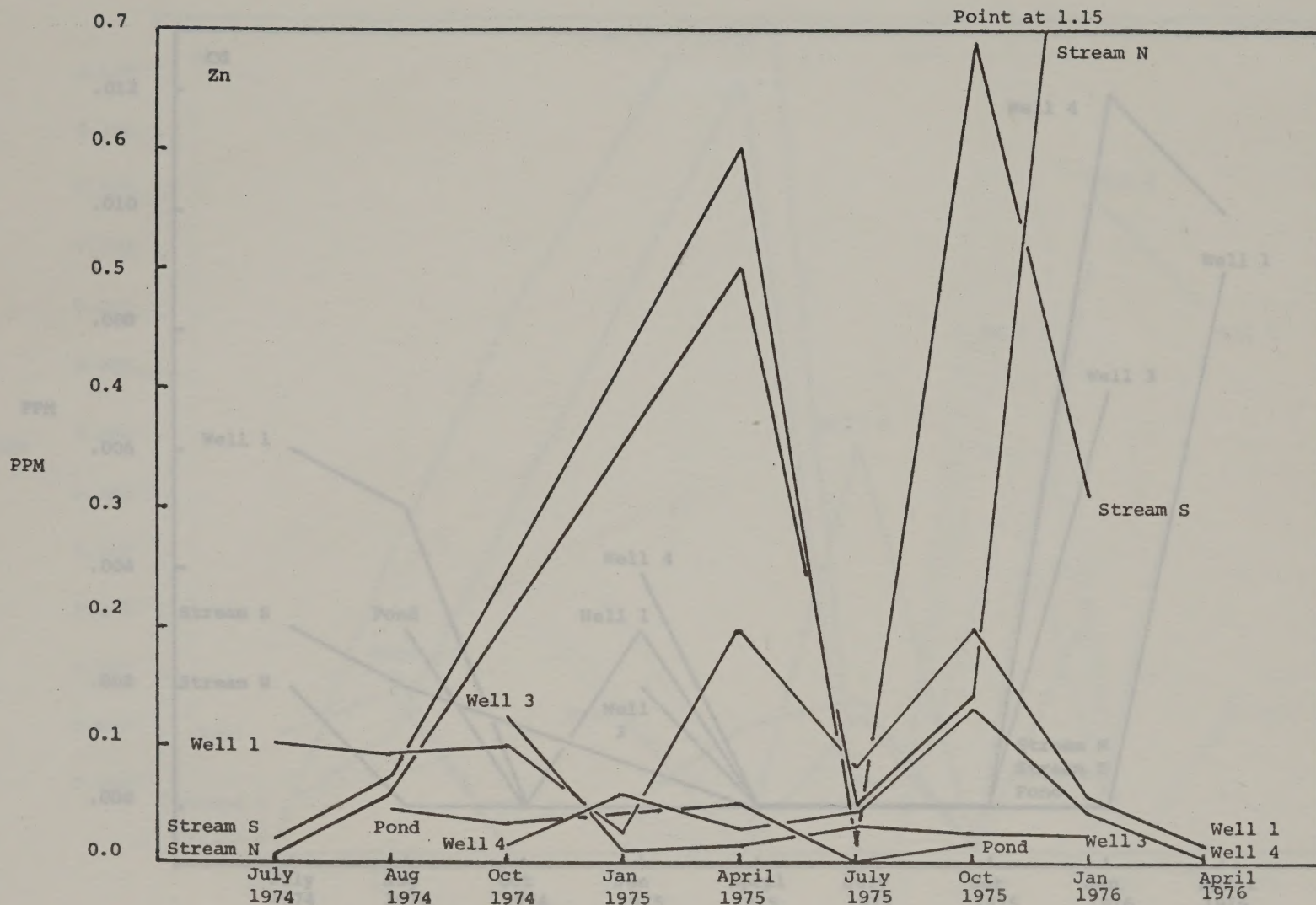




FIGURE IV-8-12  
SING

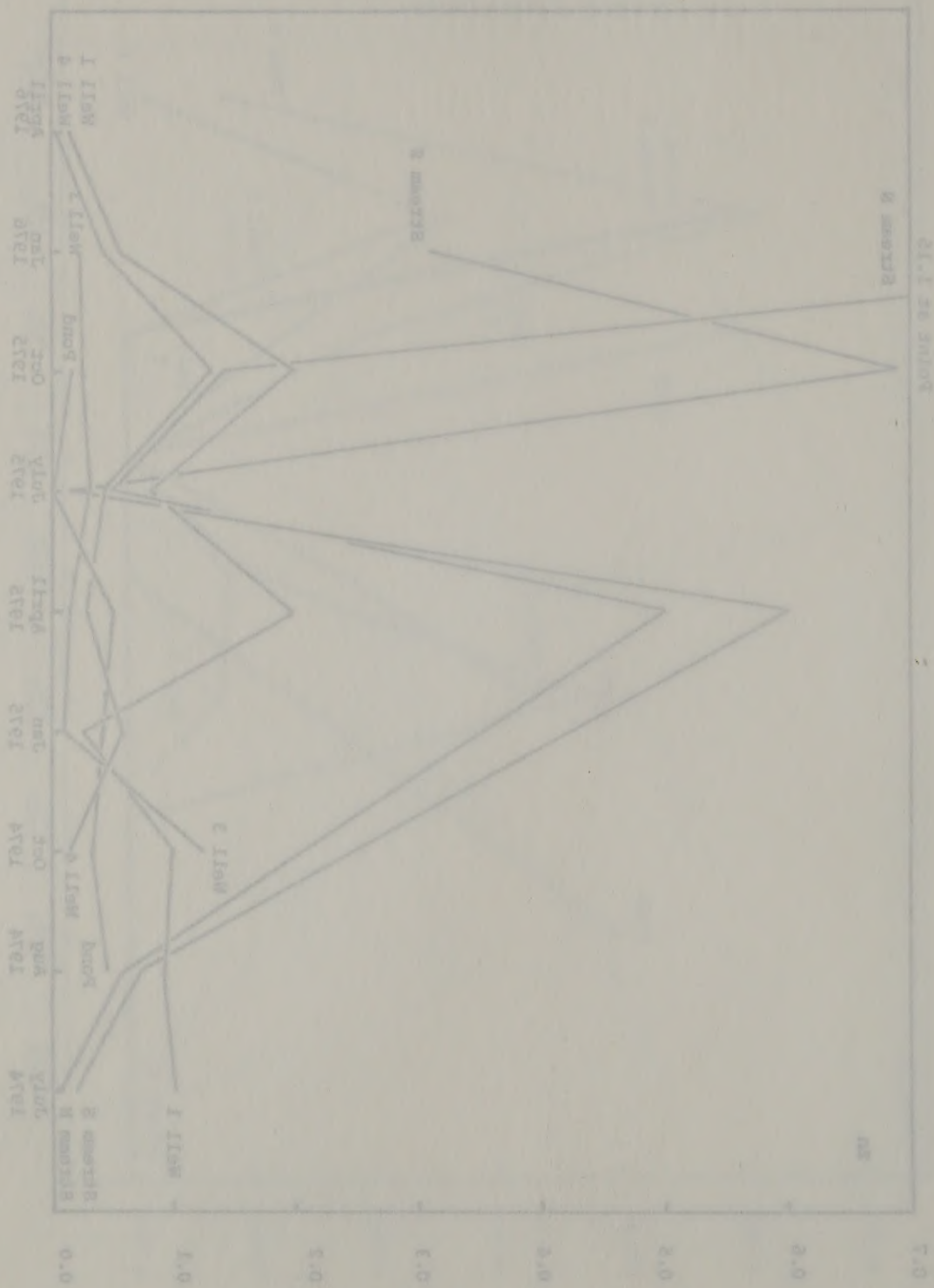


FIGURE IV-B-16  
CADMIUM

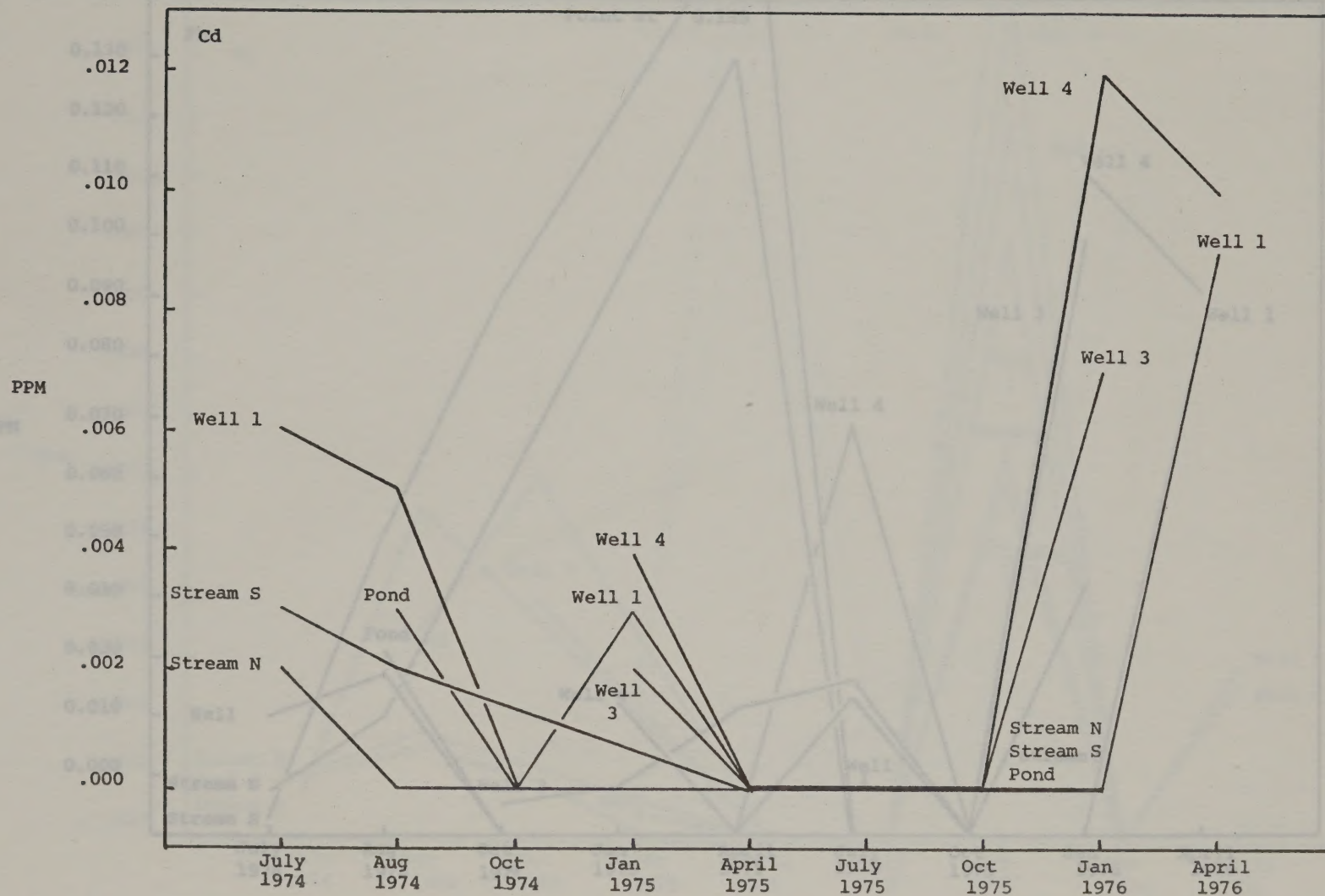






FIGURE IV-B-17  
LEAD

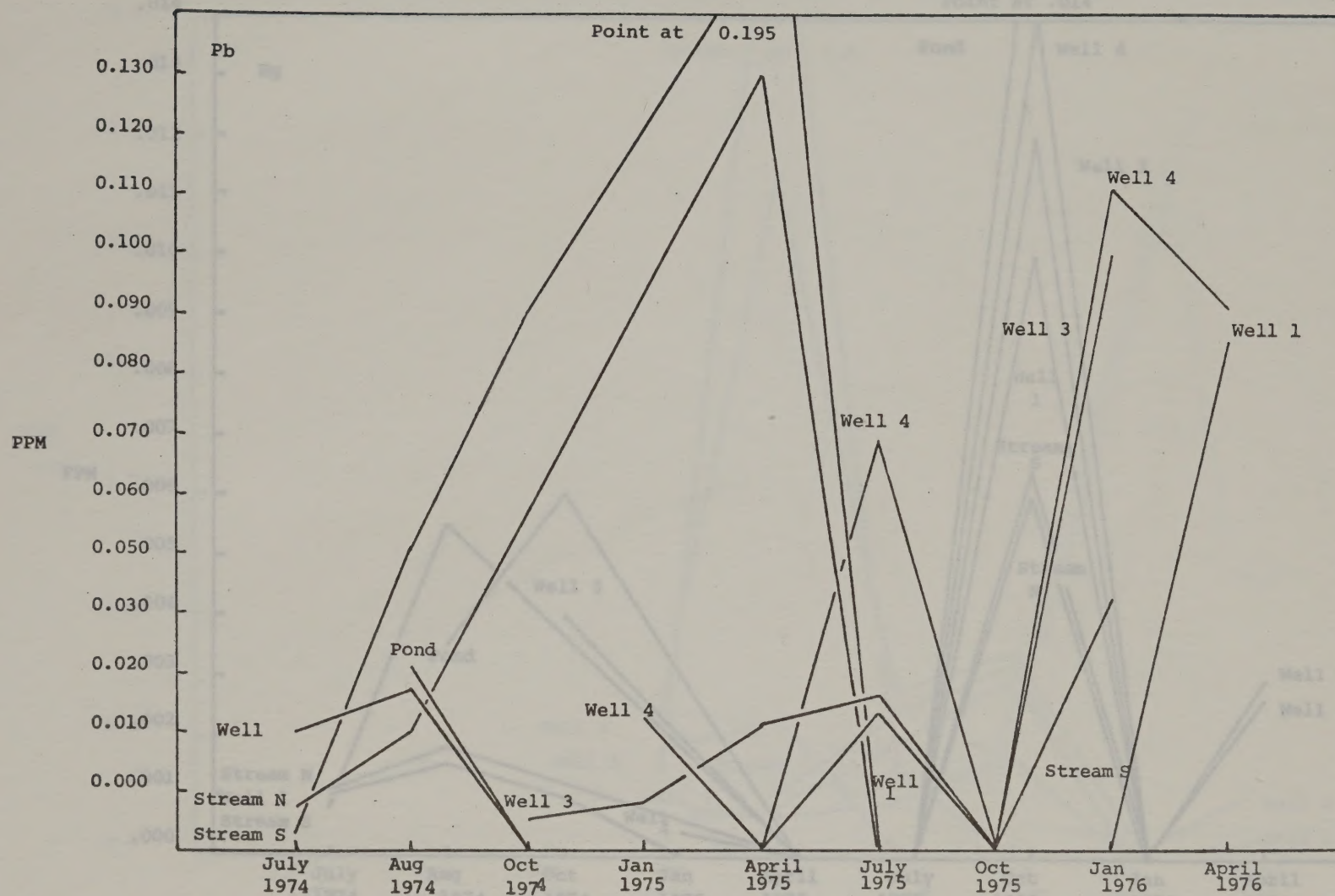




FIGURE 1A-B-17

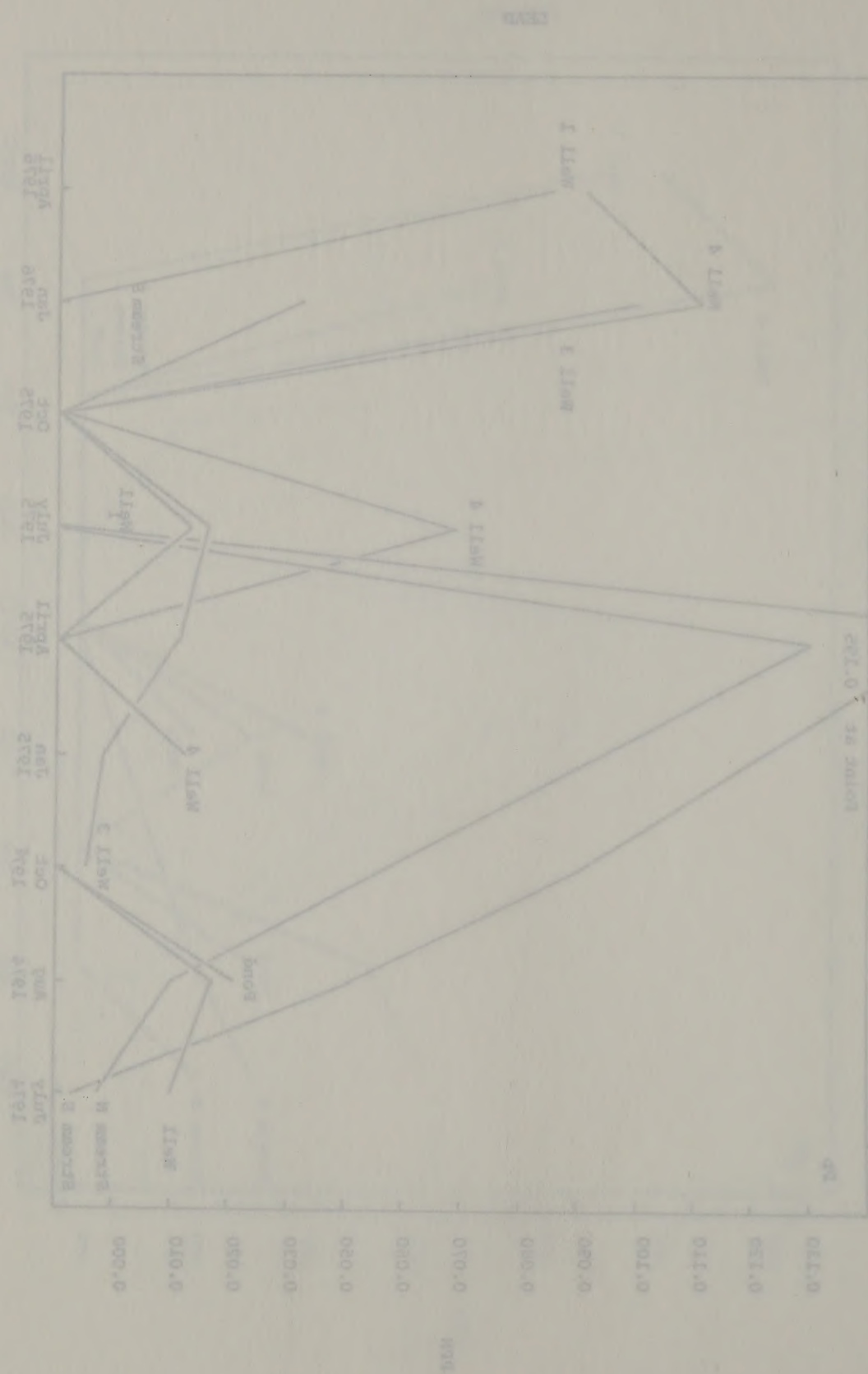


FIGURE IV-B-18  
MERCURY

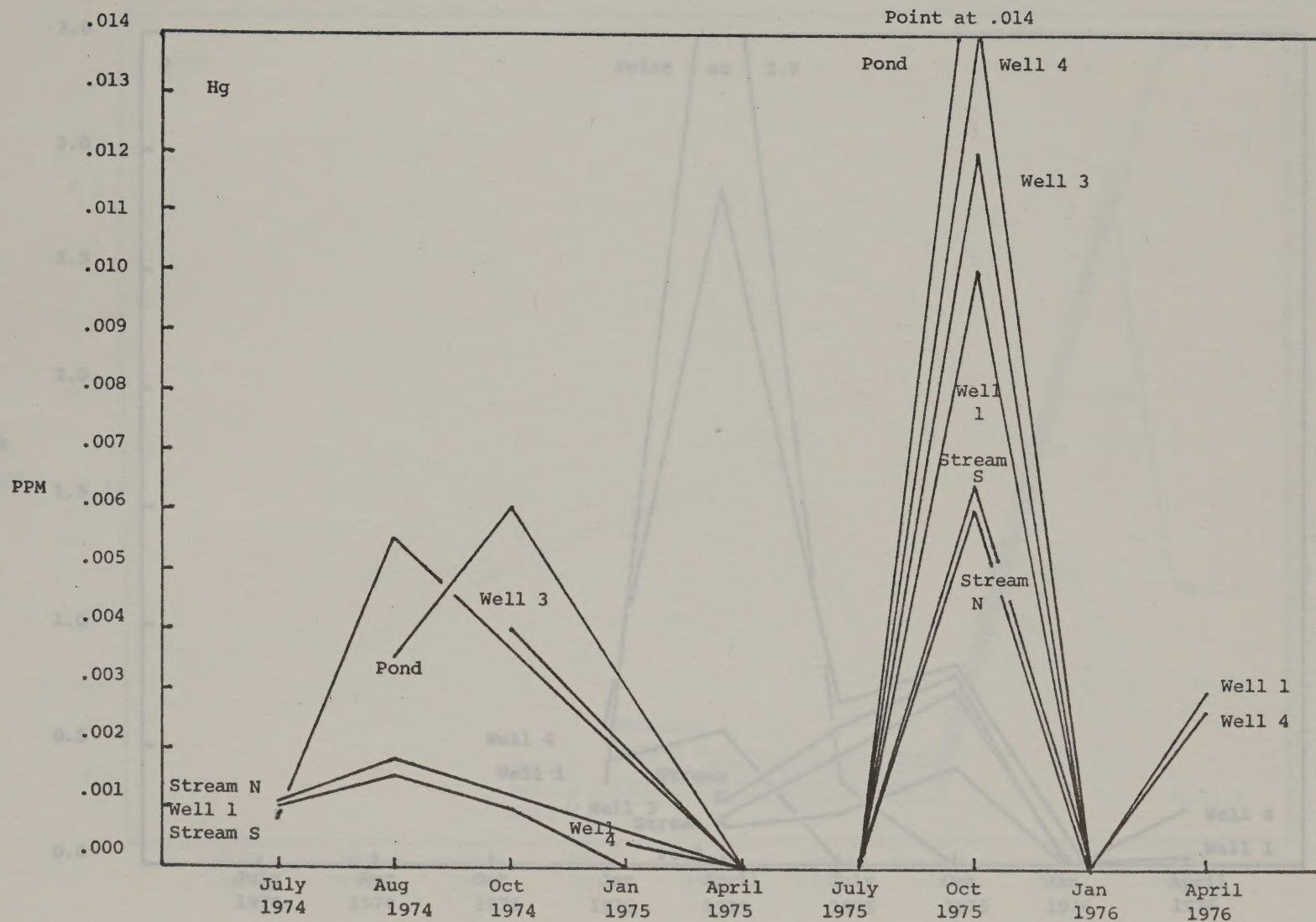




FIGURE IV-8-12  
MERCURY

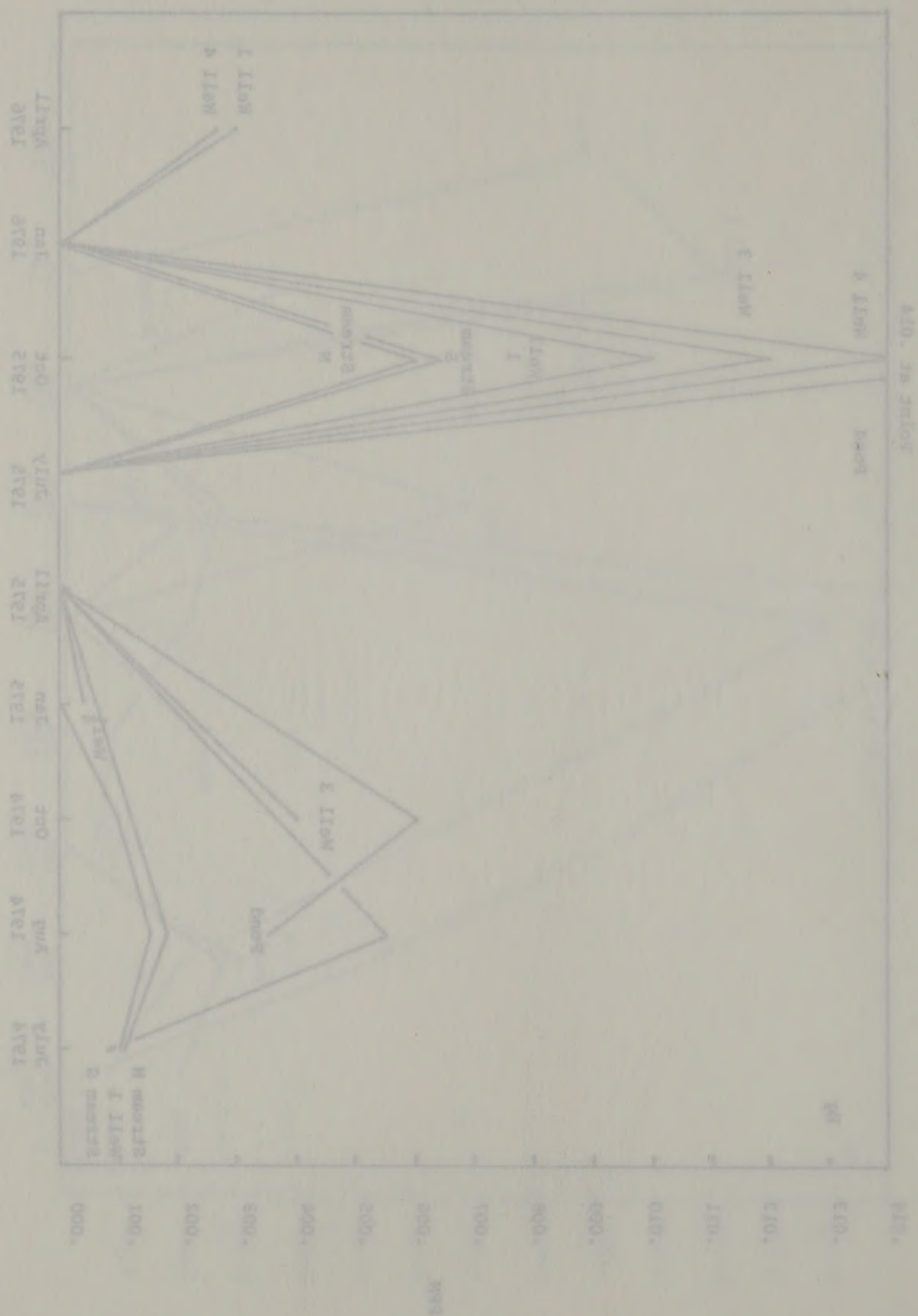


FIGURE IV-B-19

BORON

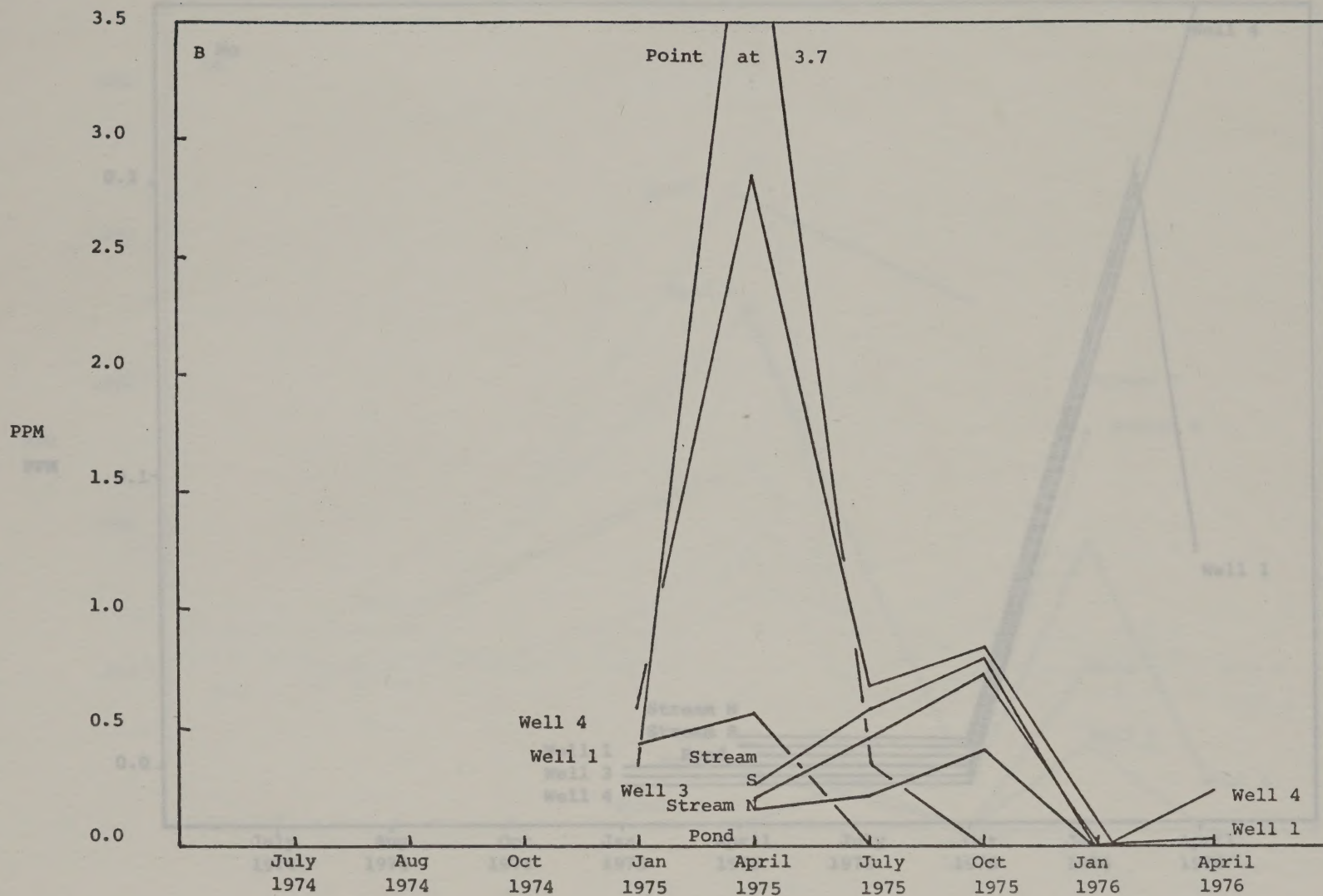






FIGURE IV-B-20  
MOLYBDENUM

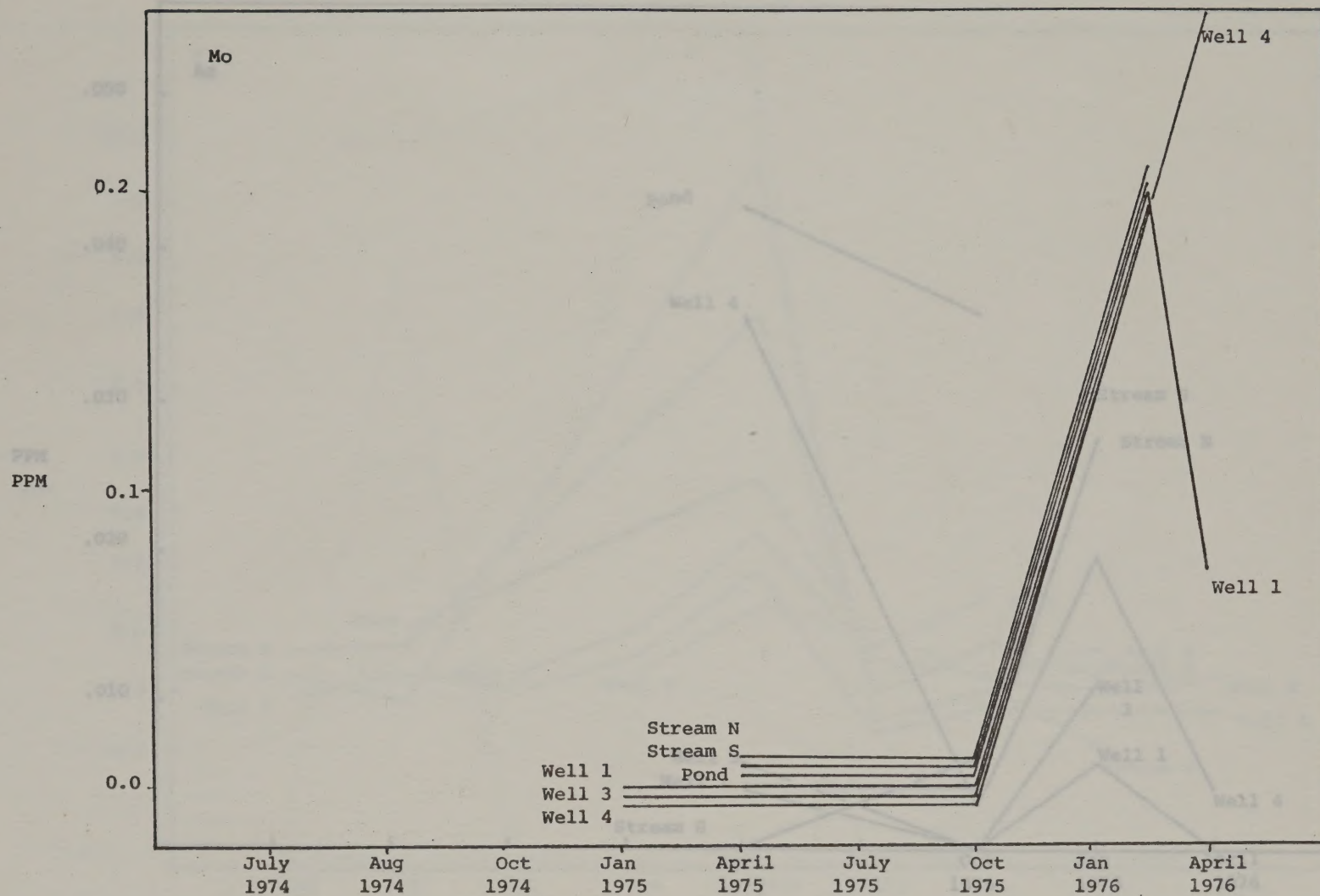






FIGURE IV-B-21  
ARSENIC

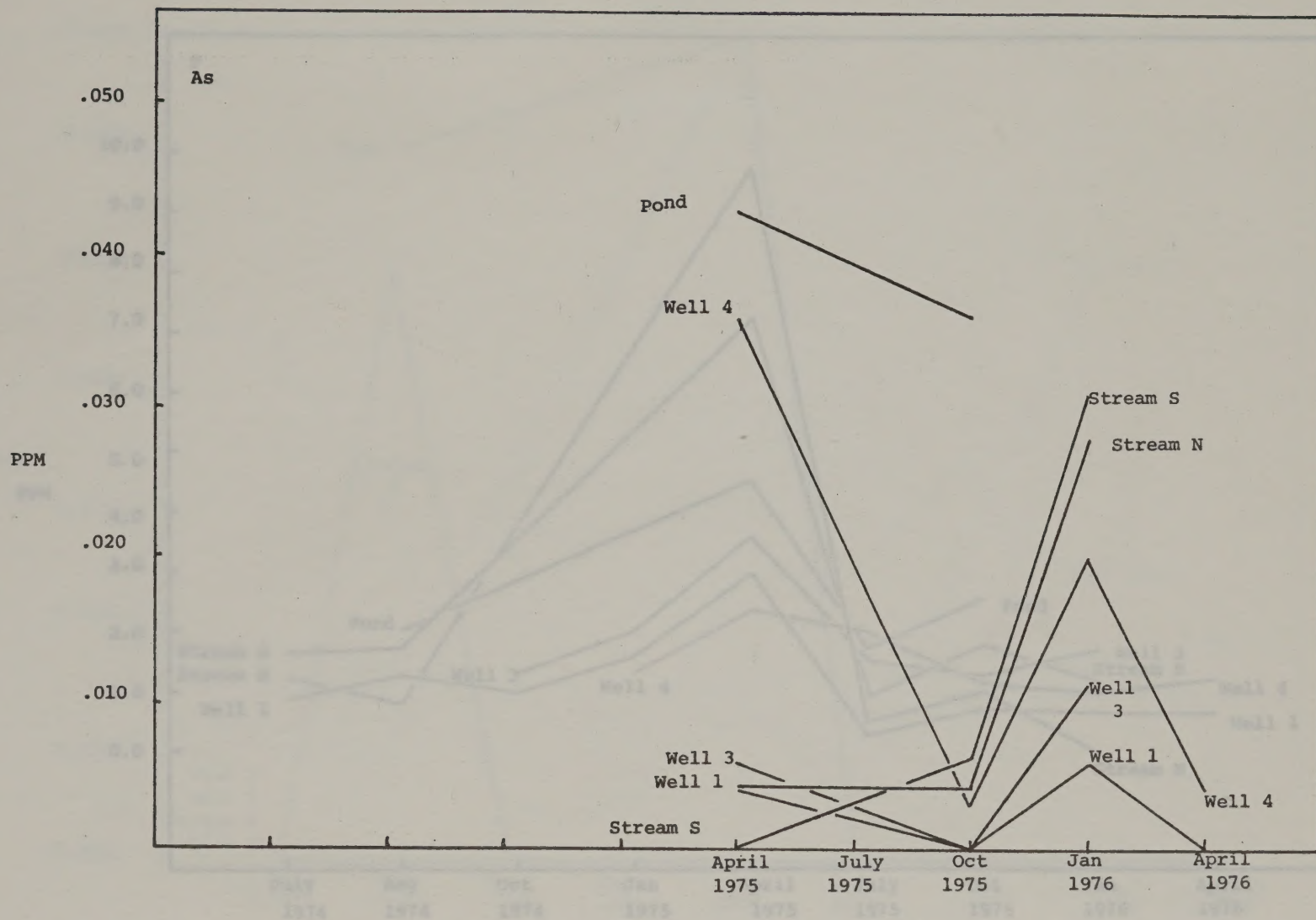




FIGURE IV-4-11  
THERMAL

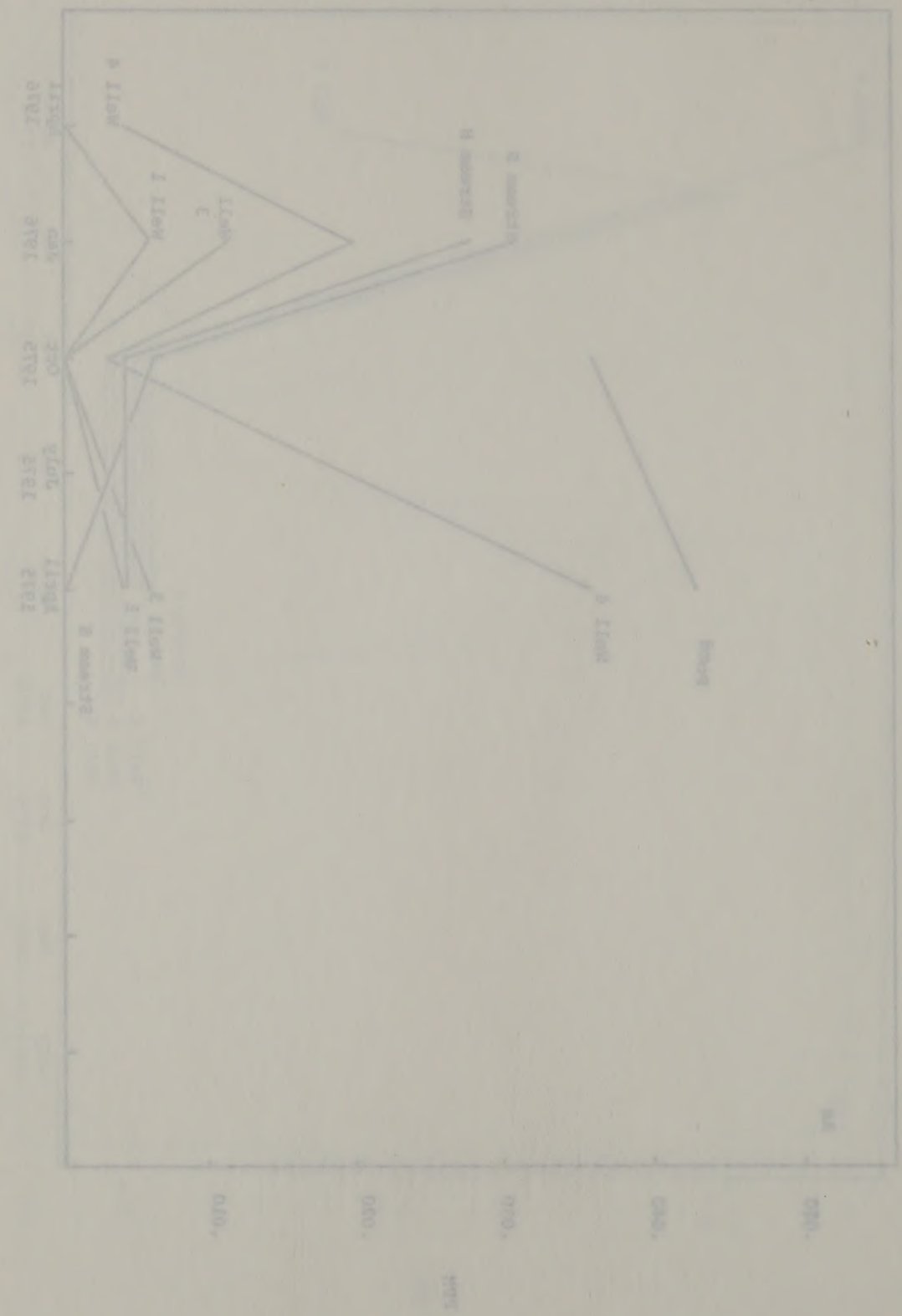


FIGURE IV-B-22  
FLUORINE

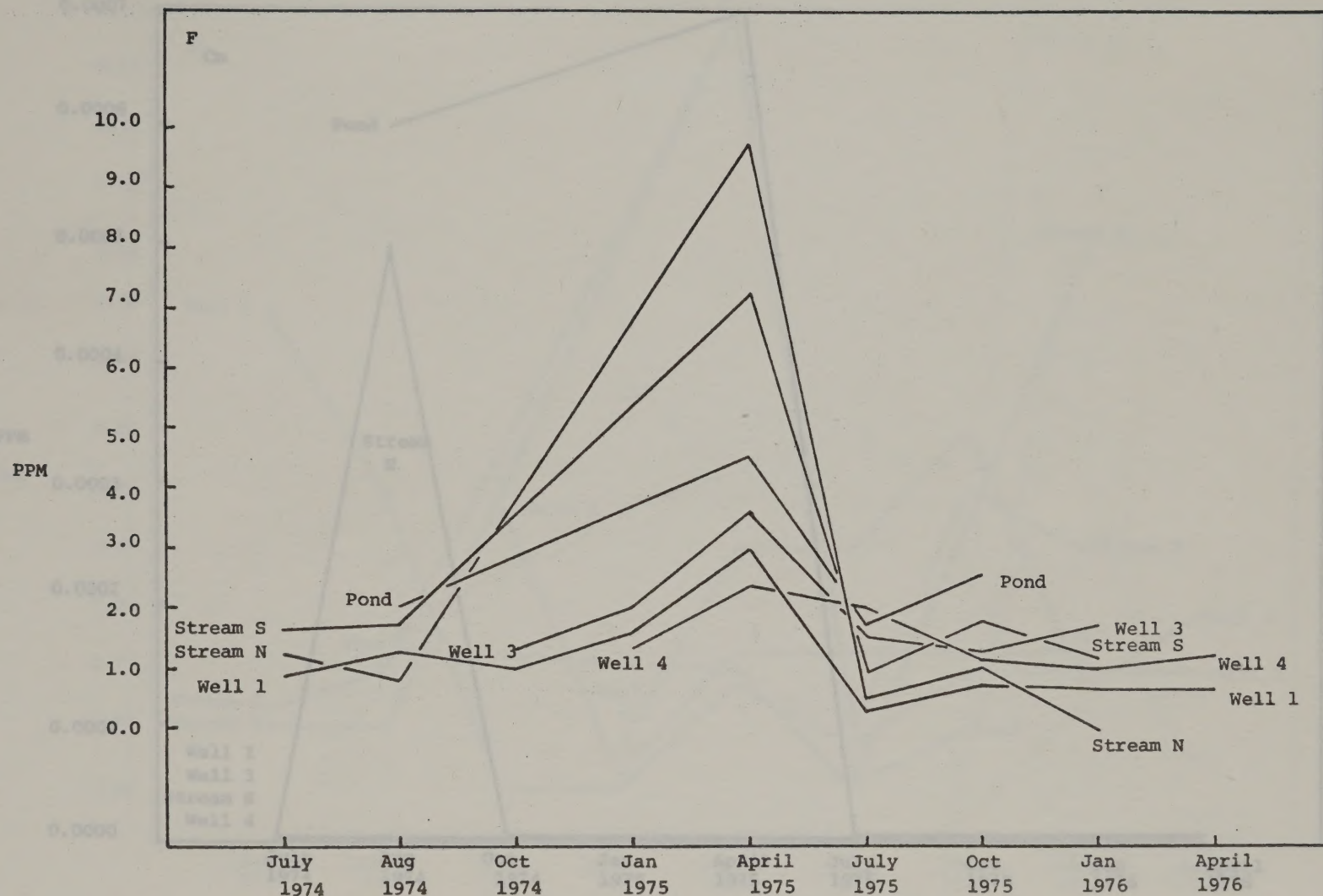




FIGURE 10-10-68

SWITCHING

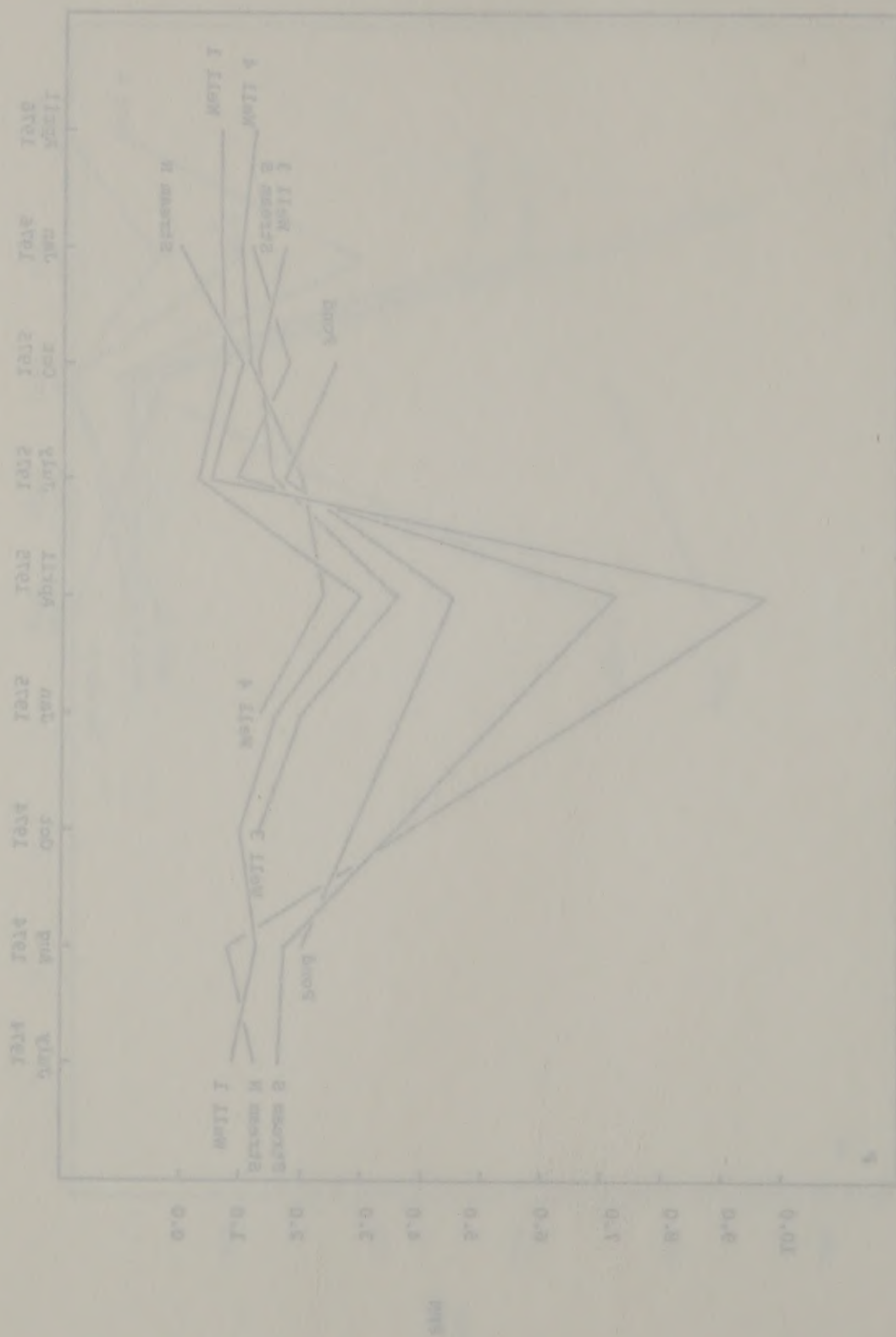


FIGURE IV-1-23  
CYANIDE

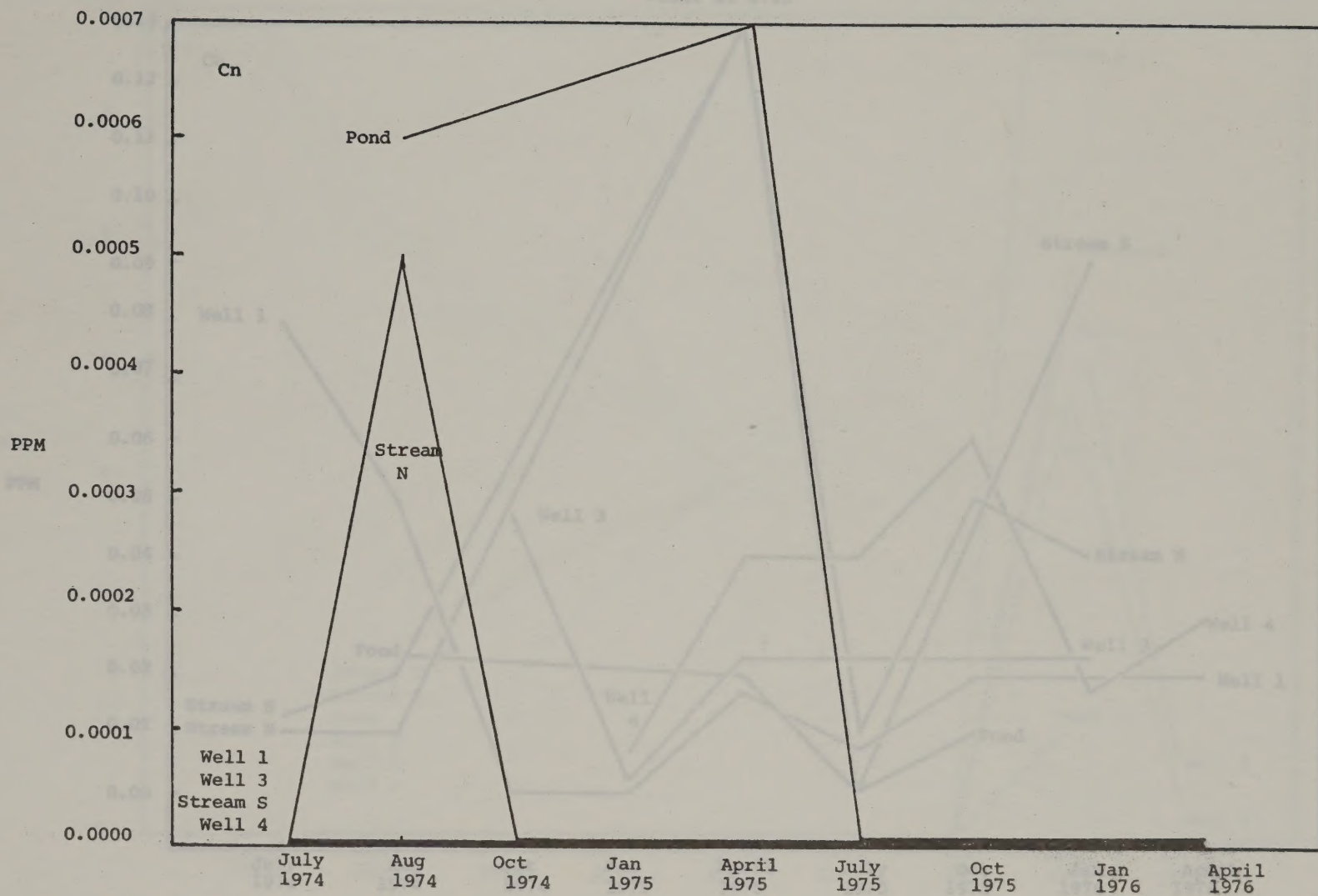




FIGURE 1A-1-31

CANYON

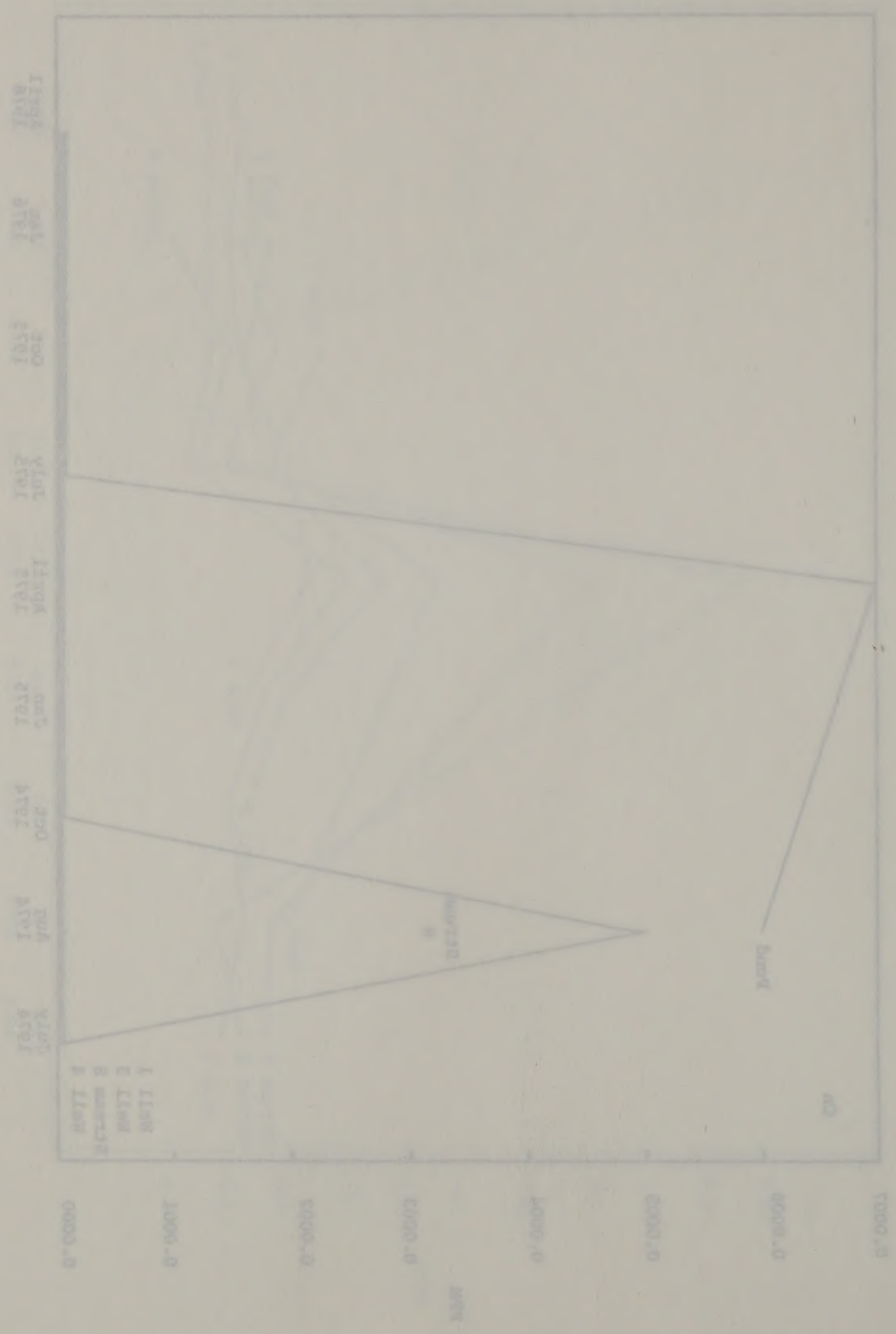


FIGURE IV-B-24  
COPPER

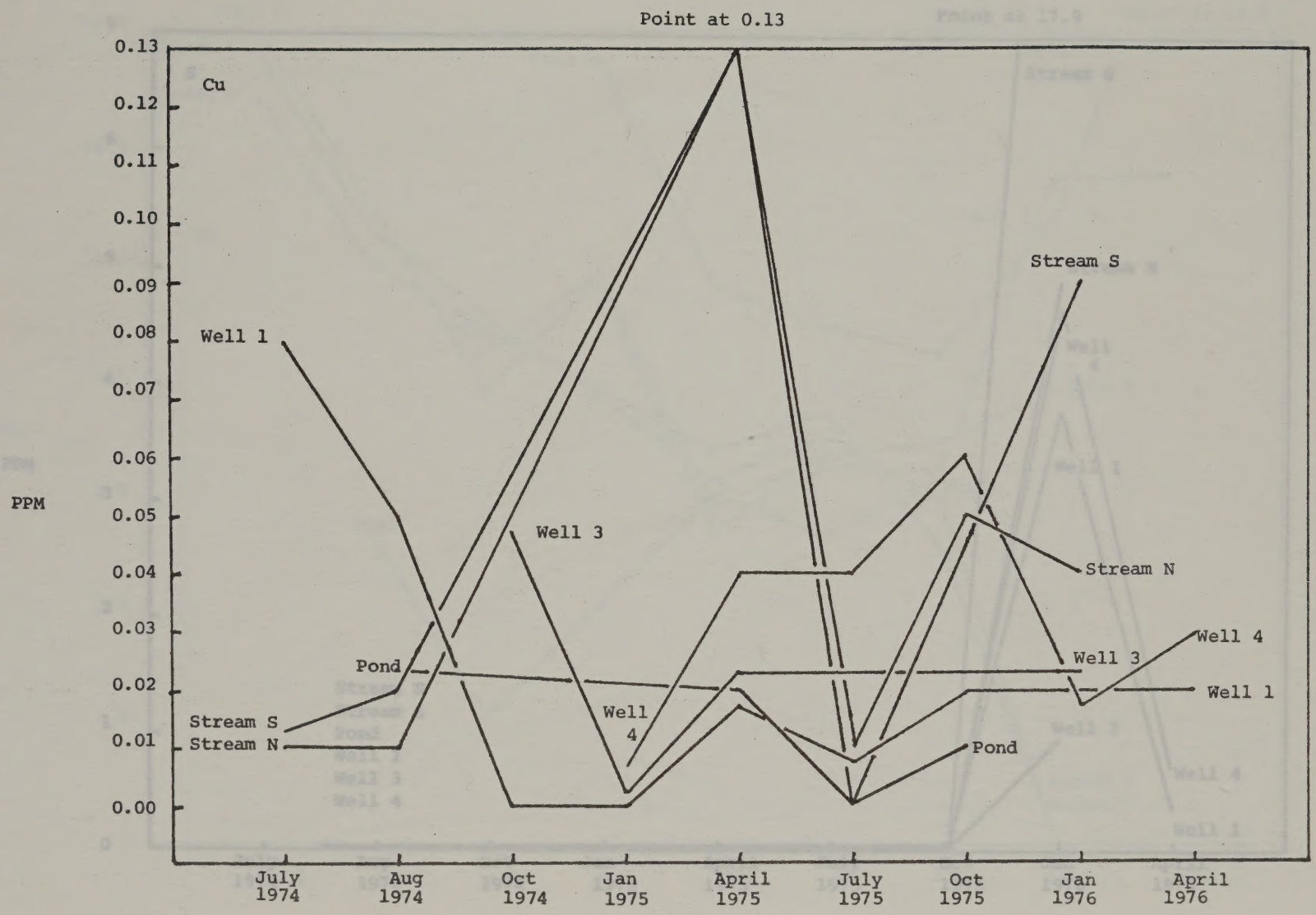




FIGURE 10-2-24

CONCRETE

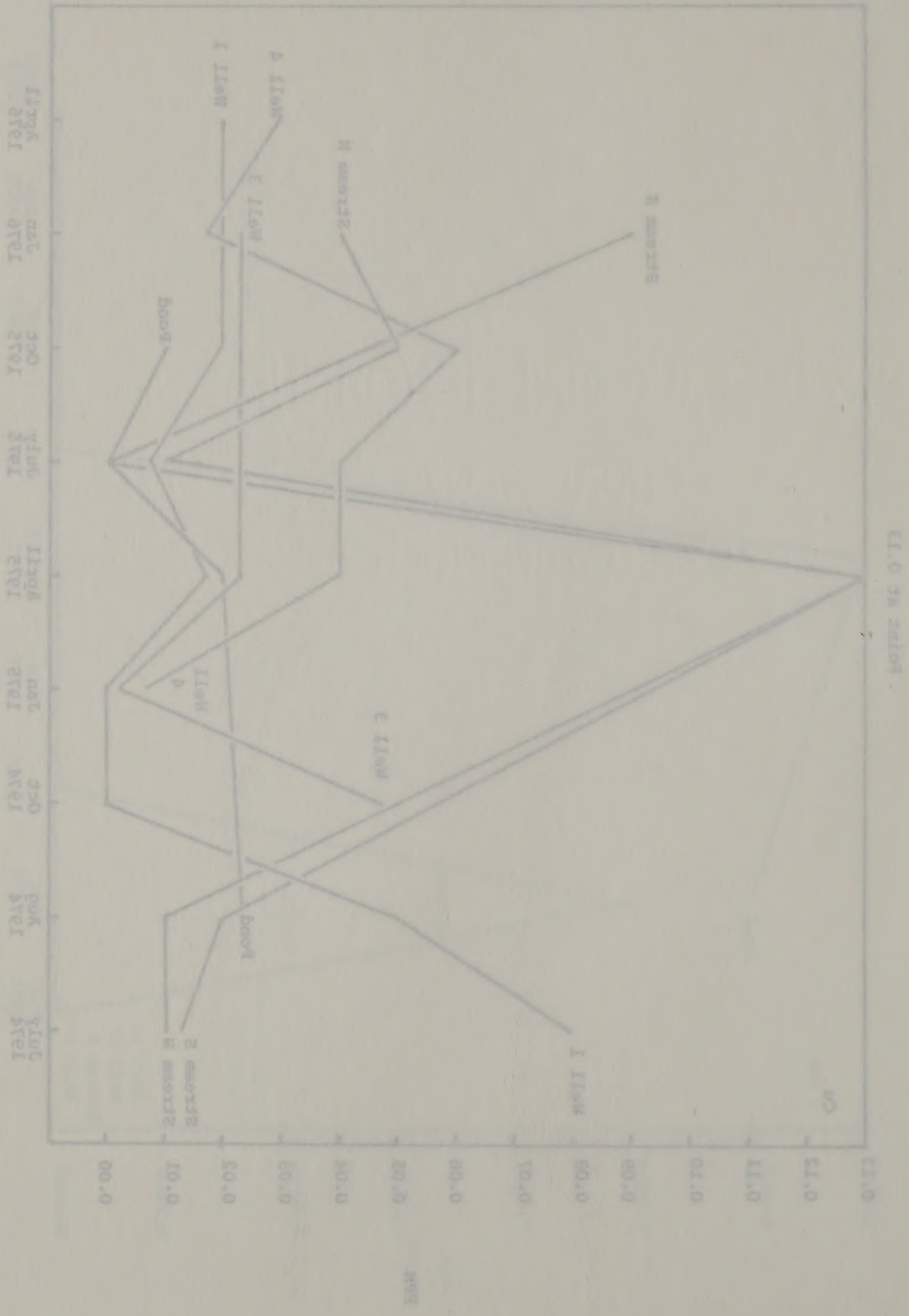
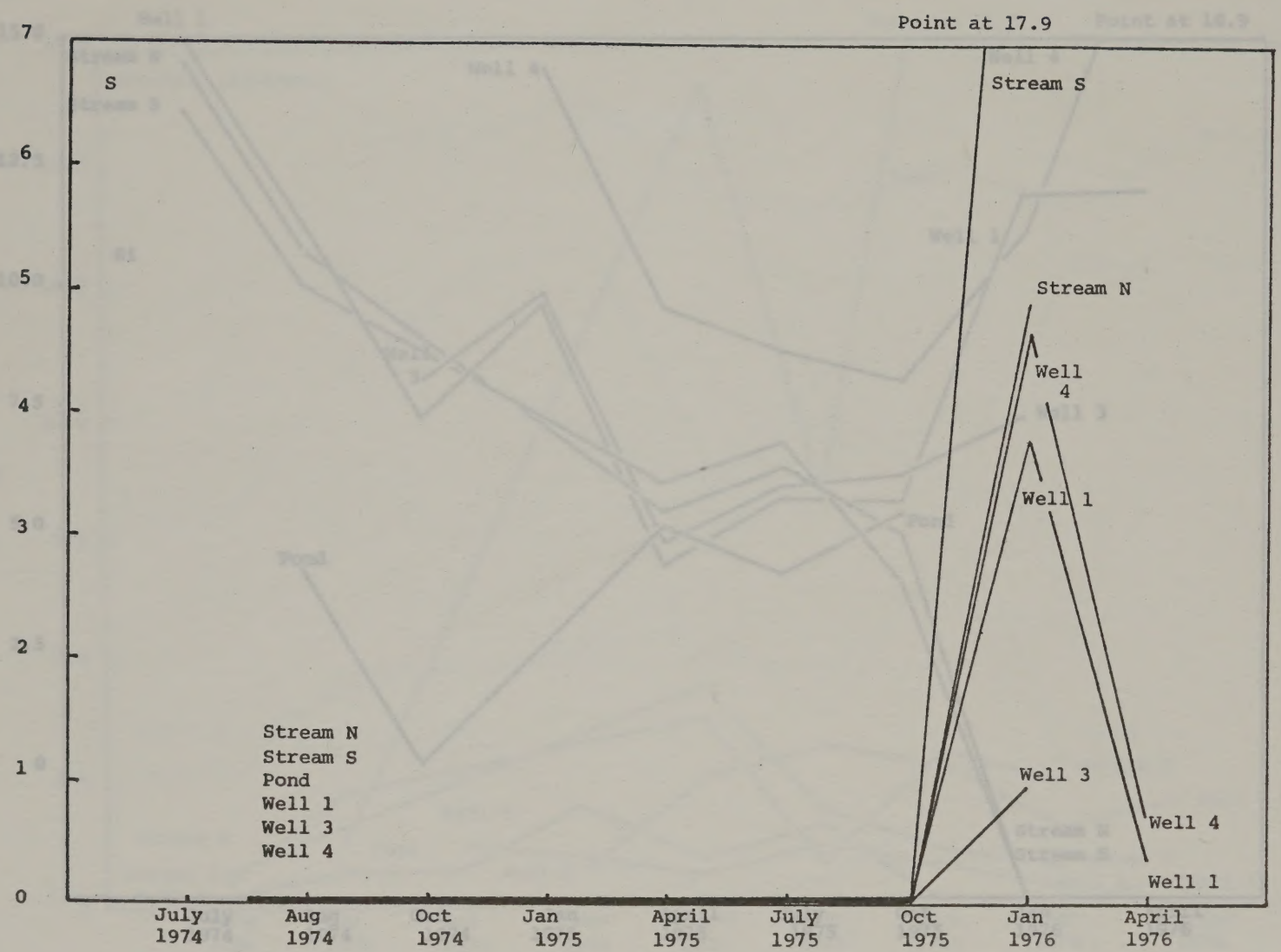


FIGURE IV-B-25  
SUFILIDE







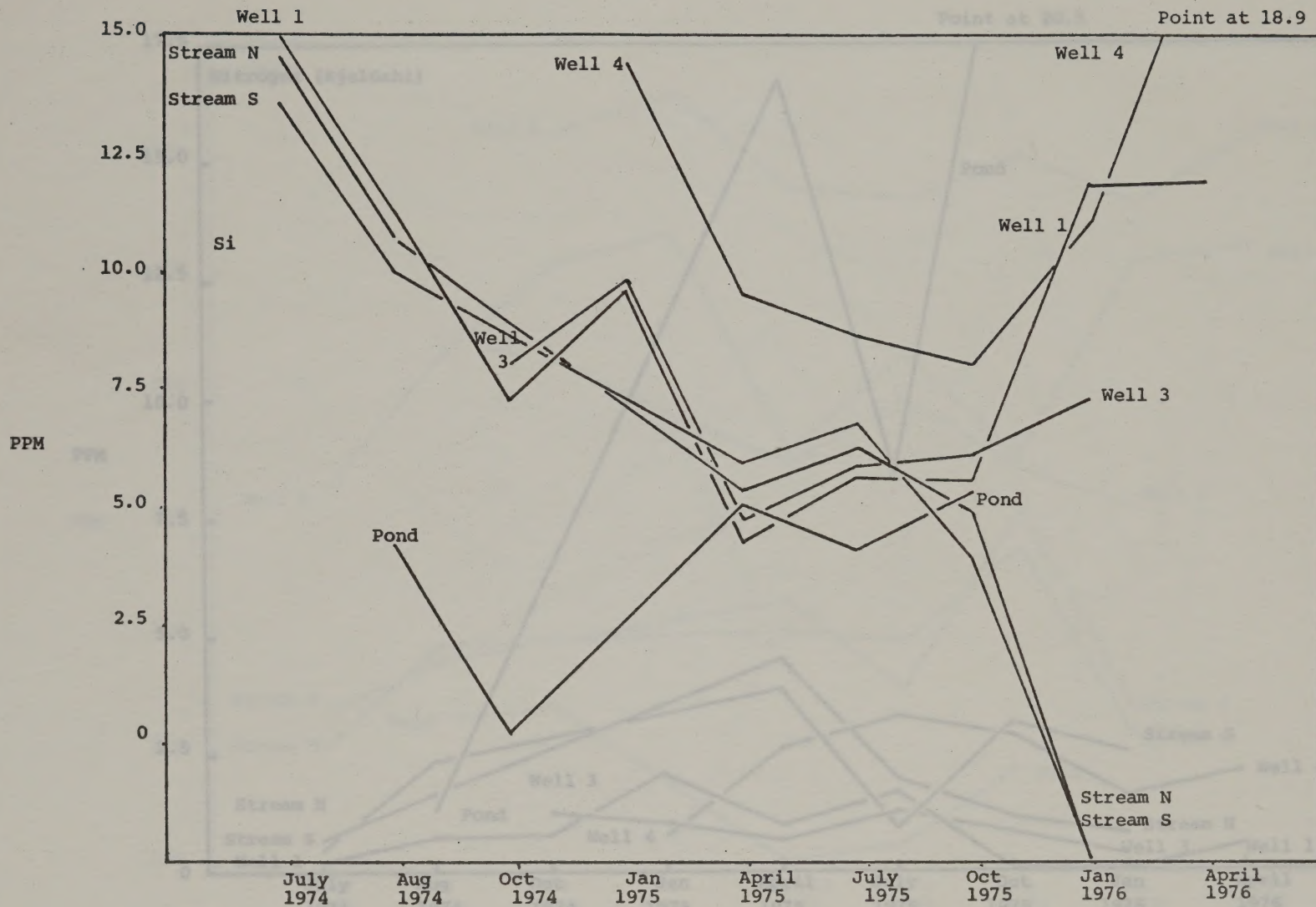


FIGURE IV-B-26  
SILICA





FIGURE IV-B-27  
KJELDHAL NITROGEN

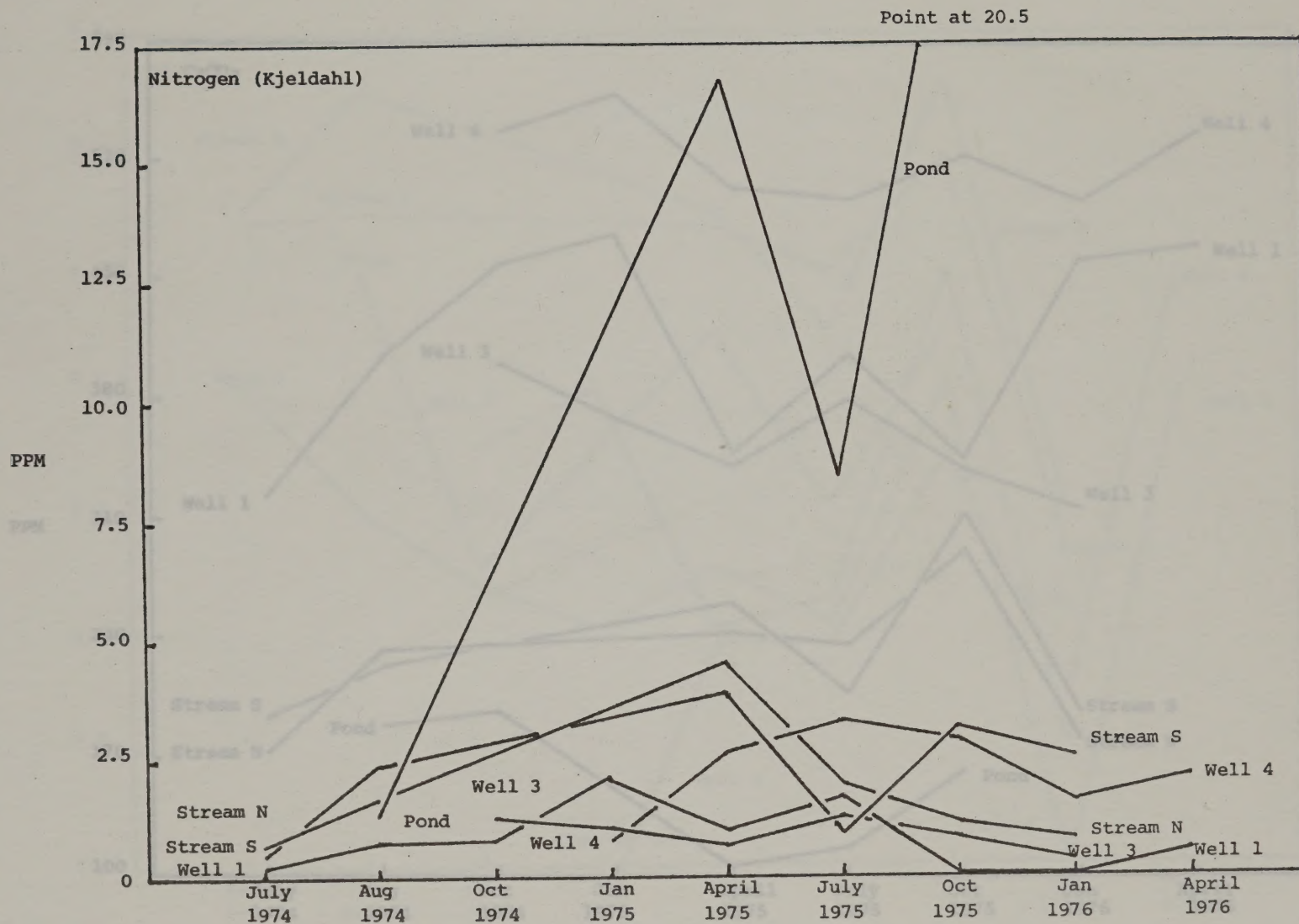






FIGURE IV-B-28  
ALKALINITY (AS  $\text{CaCO}_3$ )

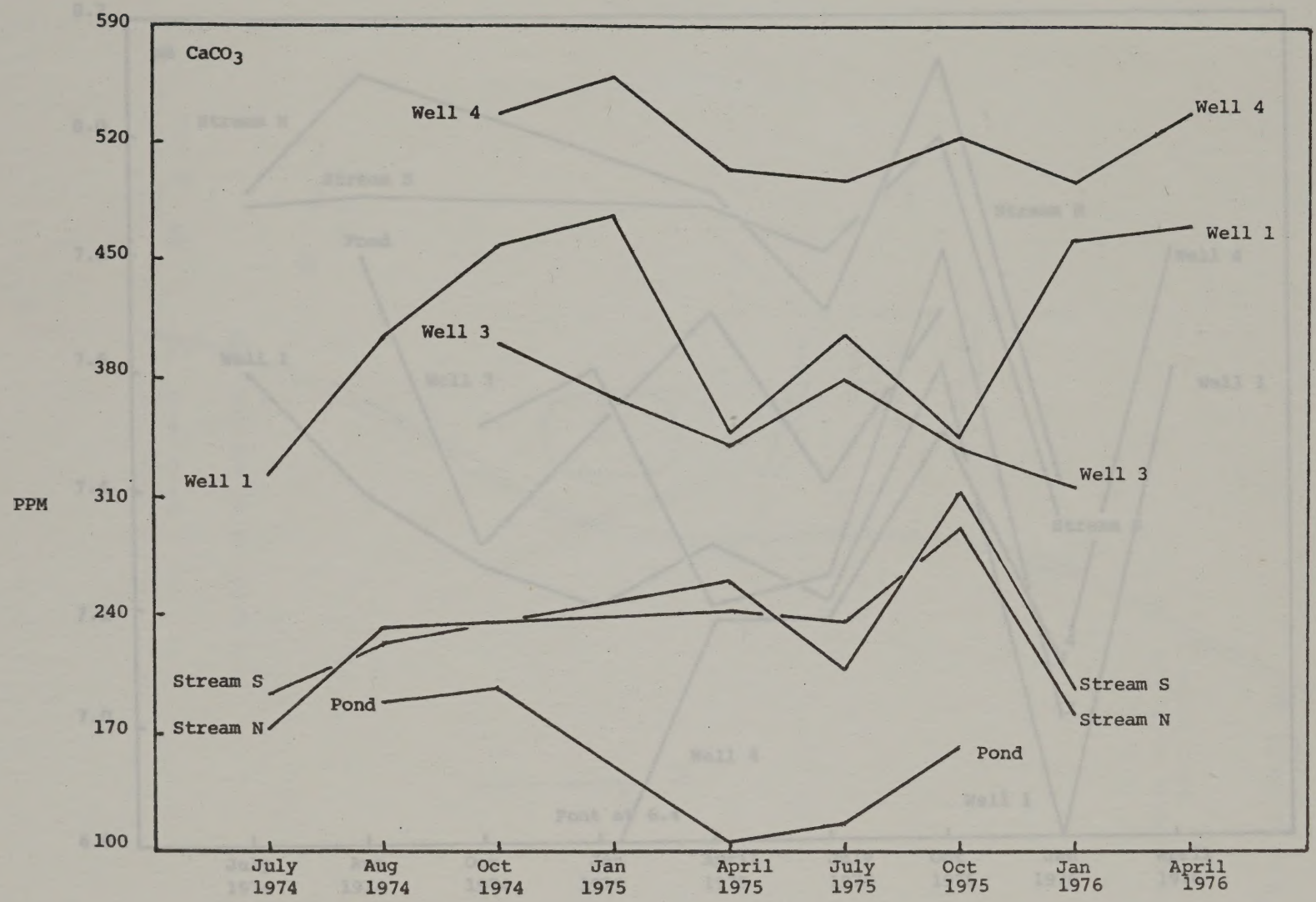
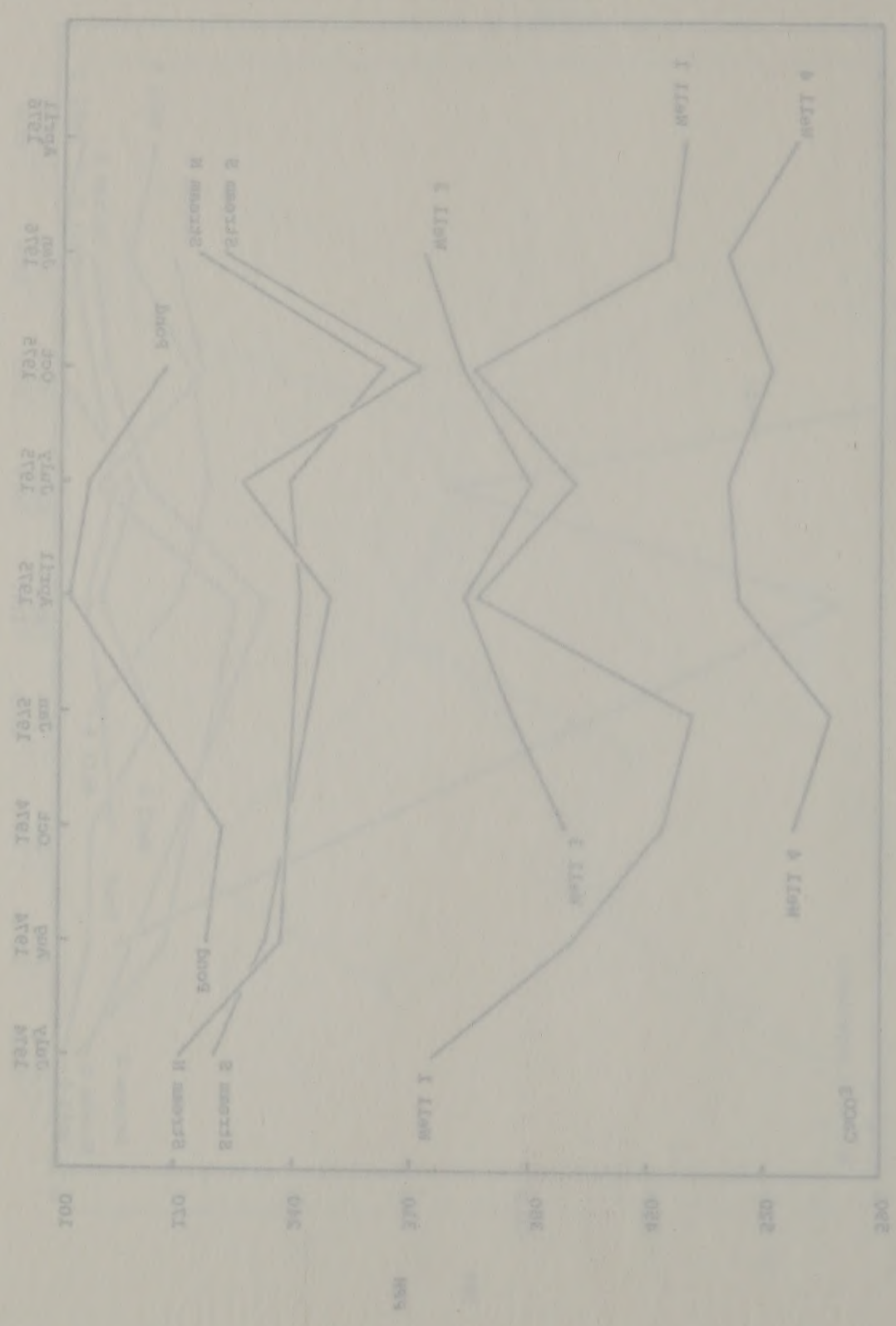




FIGURE 1A-B-38  
ALCALINITY (AS  $\text{CaCO}_3$ )



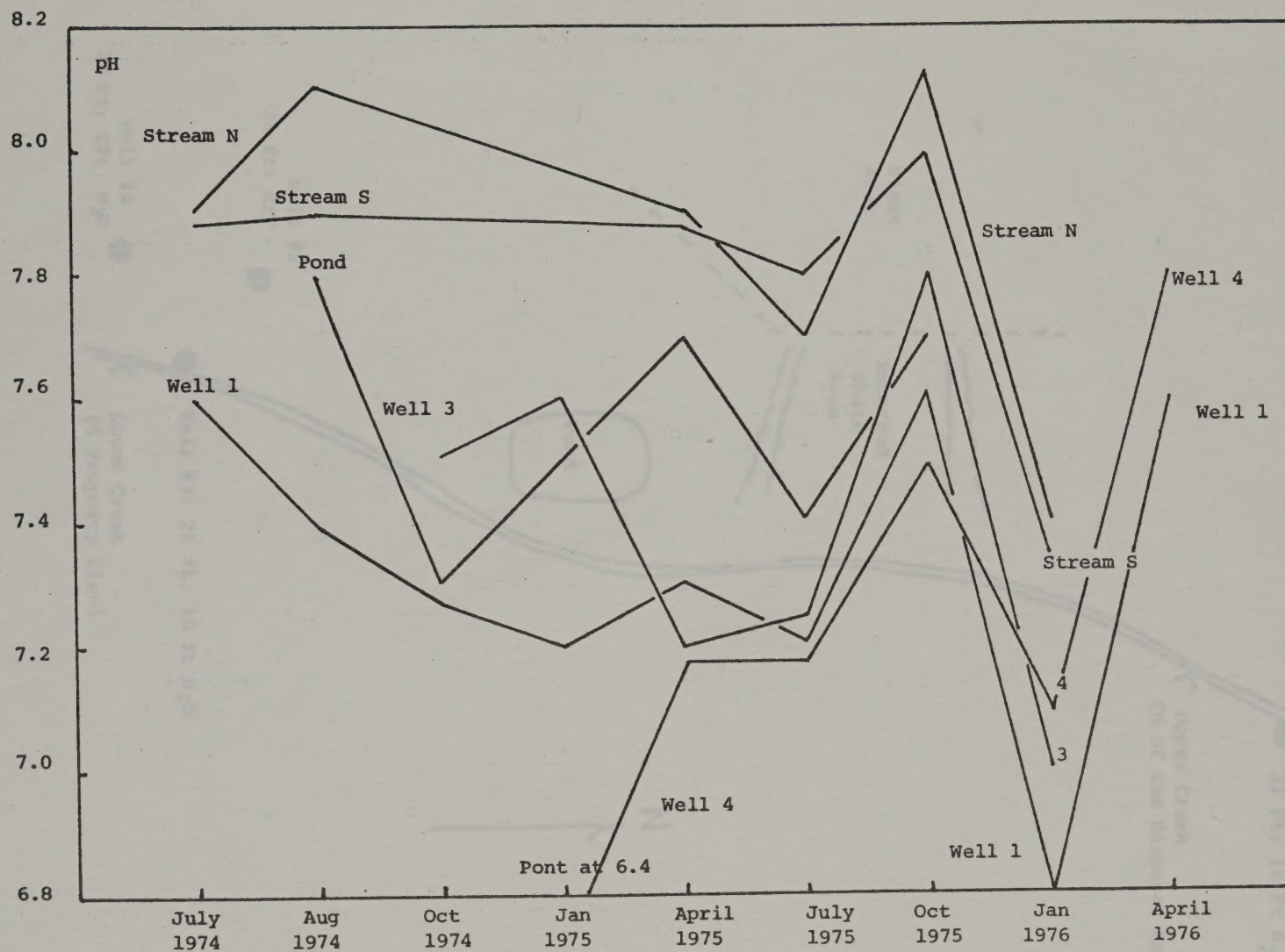


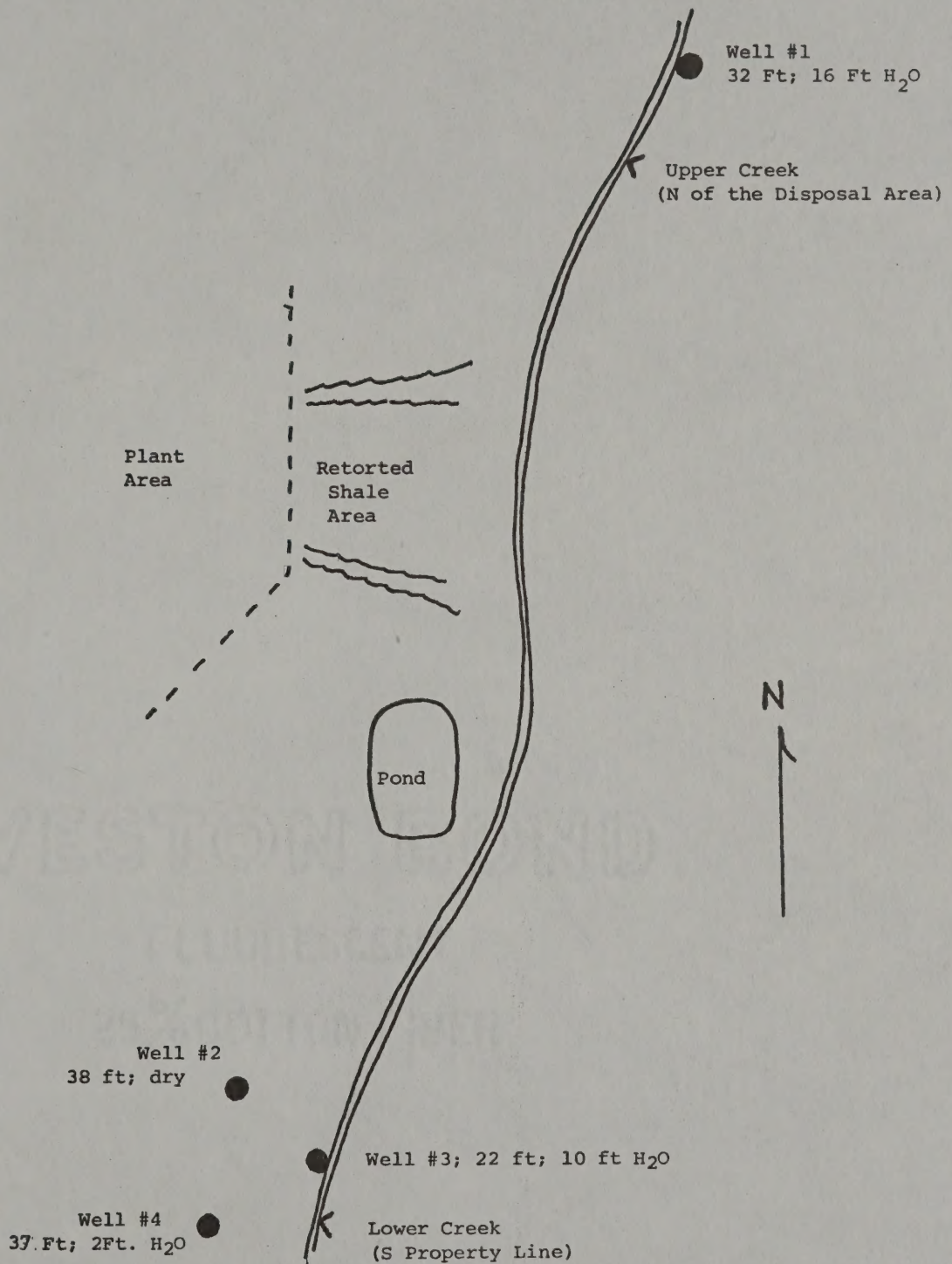
FIGURE IV-B-29  
pH





FIGURE IV-B-30

Sketch of Environmental Water Sampling Sites





1953

WESTON BOARD

CLONESTON

52% COTTON FIBER

FIGURE IVB-31  
VARIOUS STREAM SAMPLING SITES

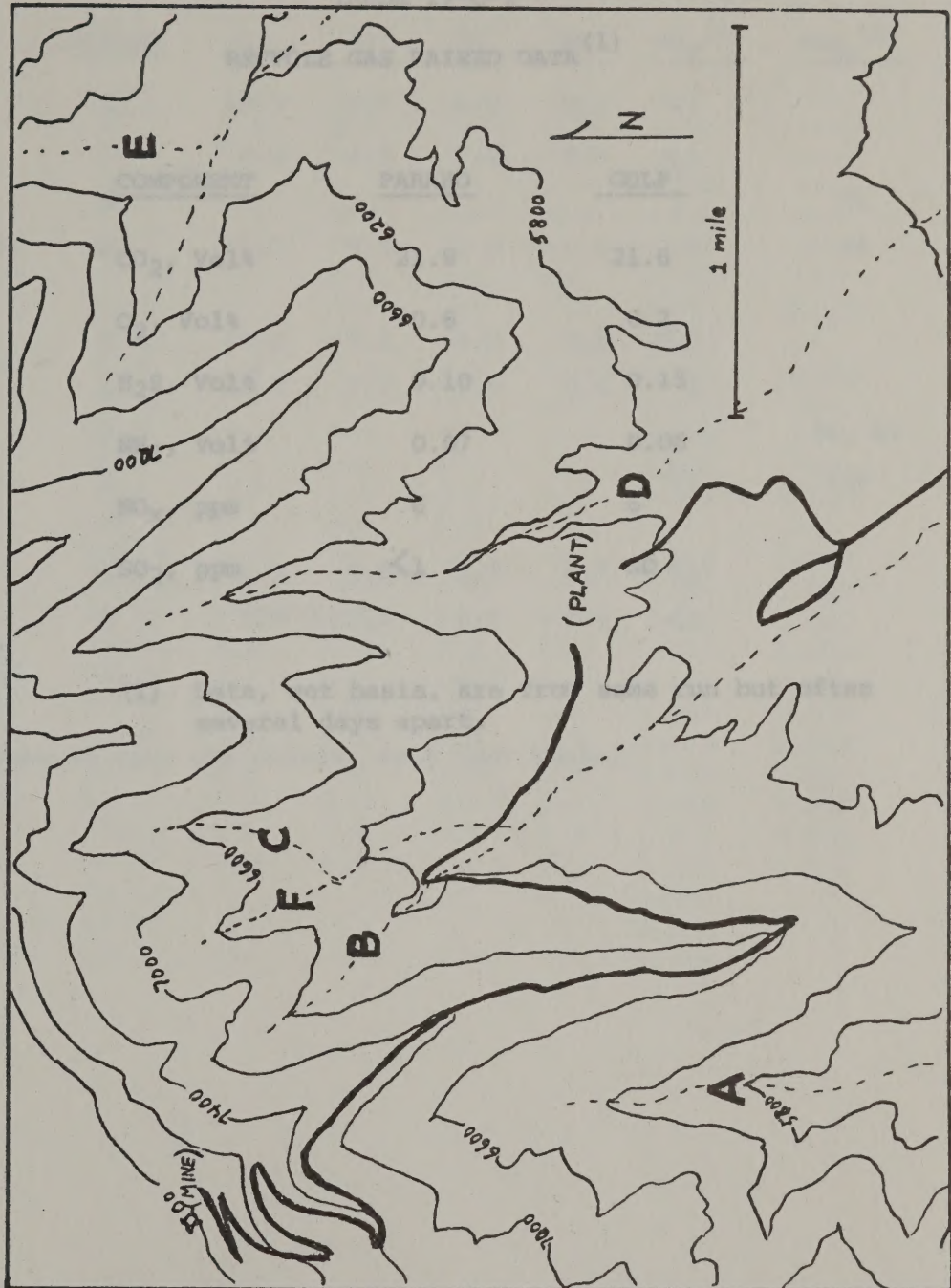




FIGURE IV-11  
VARIOUS STREAM SAMPLING SITES

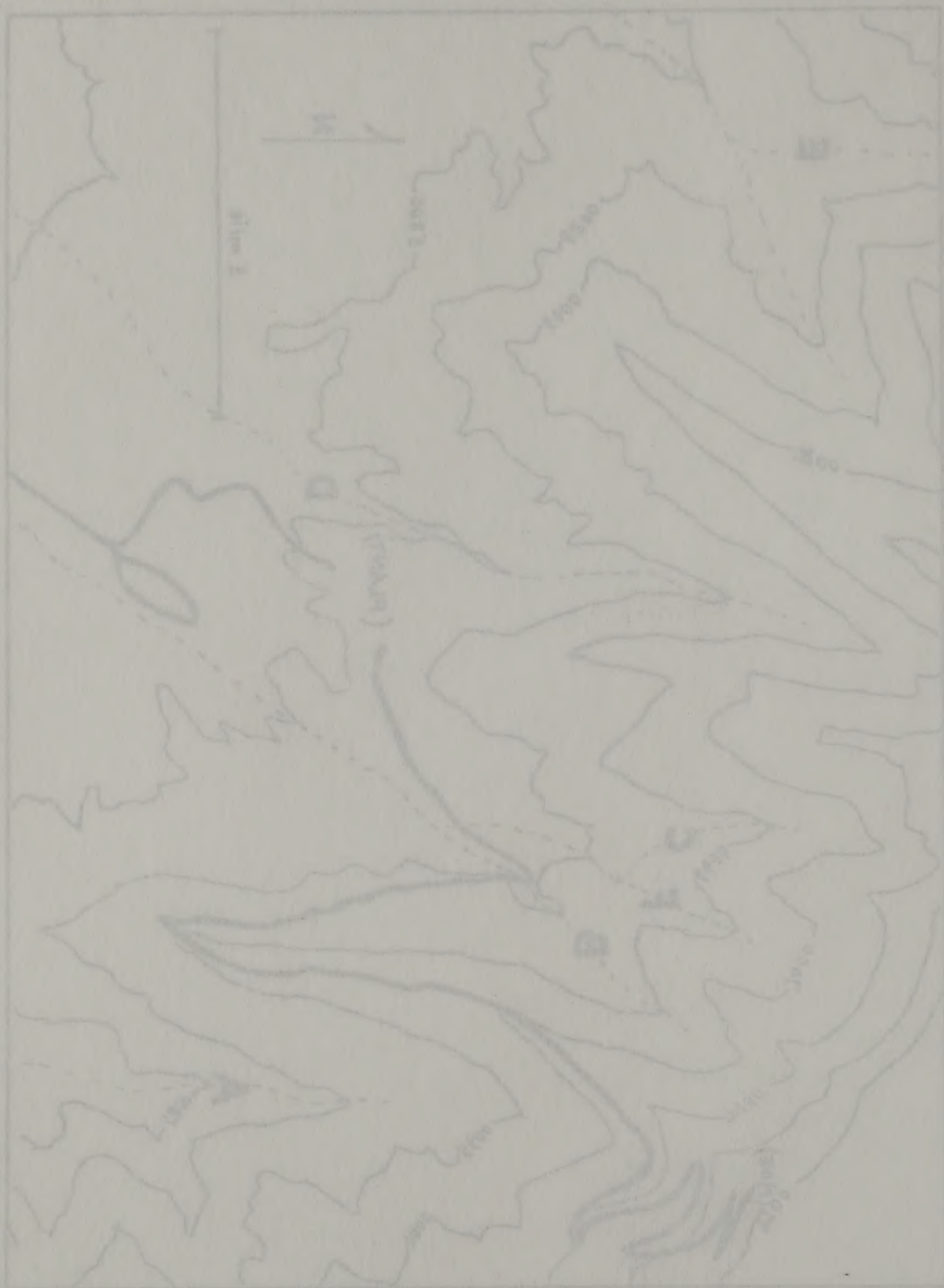


TABLE IV-C-2

BOILER STACKS

TABLE IV-C-1

DATE	BOILER	RECYCLE GAS PAIRED DATA <sup>(1)</sup>				SO <sub>2</sub> <sup>(2)</sup>	NO <sub>x</sub> <sup>(2)</sup>
3-13-75	8	10.3	5.7	0.0	0.2	<1	91
3-24-75	8	5.0	4.5	0.0	0.3	<1	91
4-10-75	8	<u>COMPONENT</u>		<u>PARAHO</u>	<u>GULF</u>		91
10-15-75	8	CO <sub>2</sub> , Vol%	21.9	21.6			94
3-13-75	8	O <sub>2</sub> , Vol%	0.6	0.7			
3-24-75	8	H <sub>2</sub> S, Vol%	0.10	0.15			
4-10-75	8	NH <sub>3</sub> , Vol%	0.07	0.06			58. 63
10-15-75	8	NO <sub>x</sub> , ppm	6	6			128
3-13-75	8	SO <sub>2</sub> , ppm	<1	ND			
3-24-75	8						

(1) Data, wet basis, are from same run but often several days apart.

(2) Values in ppm; all others, vol% (wet basis).



TABLE IV-C-1

RECYCLE GAS PAIRED DATA (1)

COMPONENT	PARAMETER	VALUE
CO <sub>2</sub> , Vol%	21.9	21.6
O <sub>2</sub> , Vol%	0.8	0.1
H <sub>2</sub> S, Vol%	0.10	0.12
NH <sub>3</sub> , Vol%	0.07	0.06
NO <sub>x</sub> , ppm	6	6
SO <sub>2</sub> , ppm	<1	ND

(1) Data, wet basis, are from same run but often several days apart.

TABLE IV-C-2

BOILER STACKS

Volume - Percent (Wet Basis)

DATE	BOILER	O <sub>2</sub>	CO <sub>2</sub>	CO	HC	SO <sub>2</sub> <sup>(1)</sup>	NO <sub>x</sub> <sup>(1)</sup>	NH <sub>3</sub>
3-13-75	N-5	10.3	5.7	0.0	0.2	<1		
3-24-75	N-7	8.0	4.5	0.0	0.3	<1		
4-10-75	N-7	7.7	8.9	0.0	0.0	0.012	91	
10-15-75	N-7	12.3	5.5	0.0	0.0	0.3	94	
3-13-75	S-8	10.9	5.2	0.0	0.1	<1		
3-24-75	S-8	10.1	1.7	0.0	0.4	2	0.022	
4-10-75	S-8					0.018	58, 63	
10-15-75	S-8	7.9	7.9	0.0	0.0	<1	128	
3-13-75	G-11	10.9	4.8	0.0	0.3	<1	0.017	
3-24-75	G-11	5.9	7.2	0.0	0.4	<1	0.042	
10-21-75	SW-17					0.007	0.030	
11-5-75	SW-20					0.003	0.036	
11-18-75	SW-20	11.4	7.5	0.0	0.0	0.003	0.016	0.028
11-20-75	SW-20	11.5	8.0	0.0	0.0	0.013	0.023	0.040
11-25-75	SW-20	11.7	7.0	0.0	0.0	0.021	0.022	0.015
11-25-75**	SW-20	9.8	8.6	0.0	0.0	0.026	0.026	0.026
11-26-75**	SW-20					0.019		
12-13-75	SW-21					0.023		
						0.130		

(1) Values in ppm; all others, vol% (wet basis).

\*Gulf

\*\*R.H.T.



TABLE IV-C-1

BOILER STACKS

DATE	BOILER	CO <sub>2</sub>	CO	HC	SO <sub>2</sub> (1)	NO <sub>x</sub> (2)
3-13-75	B	10.3	0.0	0.2	<1	
3-24-75	B	8.0	0.0	0.1	<1	
4-10-75	B					91
10-15-75	B	13.3	0.0	0.0	3	94
3-13-75	B	10.9	0.0	0.1	<1	
3-24-75	B	10.1	0.0	0.4	2	
4-10-75	B					58, 63
10-15-75	B				<1	138
3-13-75	C	10.9	0.0	0.1	<1	
3-24-75	C	9.9	0.0	0.4	<1	

(1) Values in ppm; all others, vol% (wet basis).

TABLE IV-C-3

THERMAL OXIDIZER STACK

Date	Run	Volume - Percent (Wet Basis)						
		O <sub>2</sub>	CO <sub>2</sub>	CO	HC	SO <sub>2</sub>	NO <sub>x</sub>	NH <sub>3</sub>
12-30-74	SW-5	9.8	6.2	0.0	0.0	---	---	---
3-5-75	SW-7	7.6	8.6	0.46	0.0	---	---	---
3-5-75	SW-7	7.2	9.6	0.18	0.0	---	---	---
3-6-75	SW-7	---	---	---	---	0.002	---	---
3-12-75	SW-7	7.7	8.9	0.0	0.0	0.012	---	---
3-12-75	SW-7	---	---	---	---	0.014	---	---
3-13-75	SW-7	---	---	---	---	0.008	---	---
5-6-75	SW-8	---	---	---	---	0.010	0.016	---
5-6-75	SW-8	---	---	---	---	0.014	---	---
5-8-75*	SW-8	7.7	8.1	0.0	0.0	0.038	0.022	---
5-9-75	SW-8	---	---	---	---	0.019	---	---
5-9-75	SW-8	---	---	---	---	0.018	---	---
5-9-75	SW-8	---	---	---	---	0.022	---	---
5-14-75*	SW-8	7.9	7.9	0.0	0.0	0.015	0.022	---
5-29-75	SW-9	8.6	8.8	0.0	0.0	---	---	---
7-21-75	SW-10	---	---	---	---	0.026	0.017	---
7-30-75	SW-14-4	---	---	---	---	0.005	0.022	---
8-22-75	SW-11	8.0	11.3	0.0	0.0	0.010	0.042	---
8-26-75	SW-11	11.0	7.9	0.0	0.0	0.017	0.030	---
10-21-75	SW-17	---	---	---	---	0.007	0.030	---
11-5-75	SW-20	---	---	---	---	0.003	0.036	---
11-11-75	SW-20	11.4	7.6	0.0	0.0	0.003	0.016	0.028
11-13-75	SW-20	11.6	7.8	0.0	0.0	0.013	0.023	0.040
11-18-75	SW-20	11.5	8.0	0.0	0.0	0.021	0.022	0.015
11-20-75	SW-20	11.7	7.0	0.0	0.0	0.010	0.028	0.026
11-25-75	SW-20	9.8	8.6	0.0	0.0	0.026	0.026	0.012
11-25-75**	SW-20					0.019		
11-26-75**	SW-20					0.033		
12-13-75	SW-21	---	---	---	---	0.120		

\*Gulf

\*\*R.M.T.



TABLE IV-C-3

THERMAL OXIDIZER STACK

Volume - Percent (Wet Basis)

Date	Run	O <sub>2</sub>	CO <sub>2</sub>	CO	HC	SO <sub>2</sub>	NO <sub>x</sub>	TH <sub>3</sub>
12-30-74	SW-2	8.8	8.2	0.0	0.0	---	---	---
1-2-75	SW-7	7.8	8.8	0.48	0.0	---	---	---
1-2-75	SW-7	7.2	9.8	0.18	0.0	---	---	---
1-8-75	SW-7	---	---	---	---	0.002	---	---
1-12-75	SW-7	7.7	8.9	0.0	0.0	0.012	---	---
2-12-75	SW-7	---	---	---	---	0.014	---	---
2-13-75	SW-7	---	---	---	---	0.008	---	---
2-2-75	SW-8	---	---	---	---	0.010	0.018	---
2-8-75	SW-8	---	---	---	---	0.014	---	---
2-8-75*	SW-8	7.7	8.1	0.0	0.0	0.018	0.012	---
2-9-75	SW-8	---	---	---	---	0.018	---	---
2-9-75	SW-8	---	---	---	---	0.018	---	---
2-9-75	SW-8	---	---	---	---	0.022	---	---
2-14-75*	SW-8	7.8	7.9	0.0	0.0	0.012	0.022	---
2-18-75	SW-9	8.8	8.8	0.0	0.0	---	---	---
2-21-75	SW-10	---	---	---	---	0.026	0.017	---
2-21-75	SW-14-2	---	---	---	---	0.002	0.022	---
2-22-75	SW-11	8.0	11.2	0.0	0.0	0.010	0.042	---
2-26-75	SW-11	11.0	7.9	0.0	0.0	0.017	0.030	---
10-21-75	SW-17	---	---	---	---	0.007	0.030	---
11-2-75	SW-20	---	---	---	---	0.003	0.036	---
11-11-75	SW-20	11.4	7.8	0.0	0.0	0.003	0.016	0.028
11-13-75	SW-20	11.8	7.8	0.0	0.0	0.012	0.023	0.040
11-18-75	SW-20	11.8	8.0	0.0	0.0	0.021	0.022	0.018
11-20-75	SW-20	11.7	7.0	0.0	0.0	0.010	0.028	0.028
11-22-75	SW-20	9.8	8.8	0.0	0.0	0.028	0.028	0.012
11-28-75**	SW-20	---	---	---	---	0.018	---	---
11-28-75**	SW-20	---	---	---	---	0.022	---	---
12-13-75	SW-21	---	---	---	---	0.120	---	---

\*Gulf  
\*\*R.M.T.

TABLE IV-C-3

SEMI-WORKS HEATER STACK

TABLE IV-C-4

PILOT PLANT HEATER STACK

Date	Run No.	O <sub>2</sub>	CO <sub>2</sub>	CO	HC	SO <sub>2</sub> (1)
1-2-76	PP-21	10.4	7.6	0.0	0.0	<1
1-13-76		10.7	7.1	0.0	0.0	<1
1-14-76		10.0				
Analysis (Vol%, Wet Basis)						
Date	Run No.	O <sub>2</sub>	CO <sub>2</sub>	CO	HC	
6-12-75	PP-14	10.4	7.6	0.0	0.0	
6-19-75	PP-14	10.6	6.5	0.0	0.0	
6-20-75	PP-14	9.5	6.7	0.0	0.0	
6-30-75	PP-14	7.7	7.2	0.0	0.0	
2-21-76	PP-20	9.7	11.5	0.0	0.1	1
2-22-76		9.6	11.6	0.0	0.1	<1
3-11-76	PP-27	7.7	9.2	0.0	0.0	
3-15-76	PP-28	4.5	12.4	0.0	0.1	<1
3-16-76		5.0	11.1	0.0	0.0	<1
3-22-76		3.6	11.5	0.0	0.0	
3-23-76						510
4-4-76	PP-31					275
4-5-76		3.0	12.6	0.3	0.4	325
4-6-76		3.0	10.9	0.4	0.7	
4-7-76		4.4	13.7	0.3	0.4	475
4-8-76		4.3	13.7	0.3	0.3	165
4-9-76						582
4-9-76		5.1	11.3	0.1	0.2	505

(1) Values in ppm; all others in Vol% (Wet Basis)



TABLE IV-C-4  
ELECTRIC POWER GENERATION

Analysis (Units, Wet Basis)					Run No.	Date
HC	CO	CO <sub>2</sub>	O <sub>2</sub>			
0.0	0.0	7.6	10.4	10-14	10-14-75	10-14-75
0.0	0.0	8.3	10.6	10-14	10-14-75	10-14-75
0.0	0.0	8.7	9.3	10-14	10-14-75	10-14-75
0.0	0.0	7.7	7.7	10-14	10-14-75	10-14-75

TABLE IV-C-5  
SEMI-WORKS HEATER STACK

<u>Date</u>	<u>Run No.</u>	<u>O<sub>2</sub></u>	<u>CO<sub>2</sub></u>	<u>CO</u>	<u>HC</u>	<u>SO<sub>2</sub> (1)</u>
1-2-76	SW-23	1.2	18.0	0.0	0.0	<1
1-13-76		1.7	14.1	0.0	0.0	<1
1-14-76		1.0	14.1	0.0	0.0	<1
1-17-76		1.6	13.7	0.0	0.0	4
1-20-76		0.5	14.6	0.0	0.0	2
1-21-76		0.2	14.7	0.5	0.1	2
1-28-76		15.2	3.7	0.0	0.0	
2-2-76		1.7	12.8	0.4	0.1	<1
2-19-76	SW-24	9.2	7.9	0.0	0.0	
2-21-76	SW-25	3.7	11.5	0.0	0.1	1
2-22-76		3.6	11.6	0.0	0.1	<1
3-11-76	SW-27	7.7	9.2	0.0	0.0	
3-15-76	SW-28	4.5	11.4	0.0	0.1	<1
3-16-76		5.0	11.1	0.0	0.0	<1
3-22-76		3.6	11.5	0.0	0.0	
3-23-76						530
4-4-76	SW-31					275
4-5-76		3.0	11.6	0.3	0.6	225
4-6-76		3.0	10.9	0.4	0.7	
4-7-76		4.4	11.7	0.3	0.4	478
4-8-76		4.3	11.7	0.2	0.3	165
4-8-76						582
4-9-76		5.1	11.3	0.1	0.2	500

(1) Values in ppm; all others in Vol% (Wet Basis)



HEAVY-WEIGHT HEATER STACK

Date	Run No.	O <sub>2</sub>	CO <sub>2</sub>	CO	HC	SO <sub>2</sub> (1)
1-2-76	SW-23	1.2	18.0	0.0	0.0	<1
1-13-76		1.7	14.1	0.0	0.0	<1
1-14-76		1.0	14.1	0.0	0.0	<1
1-17-76		1.6	13.7	0.0	0.0	4
1-20-76		0.5	14.6	0.0	0.0	2
1-21-76		0.3	14.7	0.2	0.1	2
1-28-76		12.2	3.7	0.0	0.0	
2-2-76		1.7	12.8	0.4	0.1	<1
2-19-76	SW-24	8.2	7.9	0.0	0.0	
2-21-76	SW-25	2.7	12.2	0.0	0.1	1
2-22-76		2.6	11.6	0.0	0.1	<1
2-11-76	SW-27	7.7	8.2	0.0	0.0	
2-12-76	SW-28	4.2	11.4	0.0	0.1	<1
2-16-76		5.0	11.1	0.0	0.0	<1
2-22-76		2.0	11.2	0.0	0.0	
2-23-76						230
4-4-76	SW-31					272
4-5-76		2.0	11.6	0.3	0.6	232
4-6-76		2.0	10.9	0.4	0.7	
4-7-76		6.4	11.7	0.3	0.4	478
4-8-76		6.3	11.7	0.2	0.2	162
4-8-76						282
4-9-76		2.1	11.3	0.1	0.2	200

(1) Values in ppm; all others in Vol% (wet basis)

TABLE IV-C-6

OTHER EMISSION DATA FROM OUTSIDE LABS

	<u>Gulf</u>	<u>RMT</u>
Recycle Gas		
COS, ppm	None detected	
CS <sub>2</sub> , ppm	" "	
Total S, Vol%	0.14 <sup>(1)</sup>	
H <sub>2</sub> O, Vol%	20.4	
Arsine, ppm	<0.01	
Thermal Oxidizer		
H <sub>2</sub> O, Vol%	12.1	8.0
Particulates, lb/SCF (dry) (x 10 <sup>5</sup> )	0.05-1.10	1.7



TABLE IV-C-2

OTHER EMISSION DATA FROM OUTSIDE LABS

Unit	Value	Parameter
		Reycle Gas
	None detected	CO <sub>2</sub> , ppm
	" "	CH <sub>4</sub> , ppm
	0.14 (11)	Total S. Vol%
	10.4	H <sub>2</sub> O, Vol%
	<0.01	Arsenic, ppm
		Thermal Oxidizer
	12.1	H <sub>2</sub> O, Vol%
		Particulates, lb/1000 (dry)
1.7	0.05-1.18	(x 10 <sup>3</sup> )







## V. SPECIAL

This section contains reports of special laboratory activities that did not "fit" in any of the other sections. This section contains the final report of Fischer assay material balances done at Anvil Points. Also included are abstract of papers that have been accepted for publication in scientific journals or presentation at scientific meetings. Reprints will be available for anyone requesting them.

1. Only the water balance show extreme deviations ( $106.9 \pm 10.0\%$ ). The deviations result from two facts: 1. water is one of the smallest quantities ( $<7\%$ ) being balanced; 2. water requires more data (11) for balance calculations than any other.
4. As may be expected, weight balance and ash balance yield the most accurate and precise data.

### PROCEDURE

A Fischer assay is run in the usual manner (Method F-5-31) except that the evolved gas is trapped (see Figure V-A-11) and analyzed and the retorted shale retained for analysis (see Table V-A-1). Using acidified water in the gas collection bottle, about 1-2" of water vacuum is maintained throughout the assay. Twenty-nine analyses are needed to calculate nine balances: weight, ash, carbonate, kerogen, water, total C, total H, total N, and total S.

### DISCUSSION

The calculations used to determine the nine material balances are



100-100000

V. SPECIAL

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## A. FISCHER ASSAY MATERIAL BALANCES

### CONCLUSIONS

1. Nine material balances were calculated on four Fischer assays. They include: weight, ash, carbonate, kerogen, water, total carbon, total hydrogen, total nitrogen and total sulfur. All raw data and calculations are given.
2. Mean balances range from 97.2 to 106.9%; individual balances range from 90.0 to 119.5%. The need for multiple data points is obvious.
3. Only the water balance show extreme deviations ( $106.9 \pm 10.0\%$ ). The deviations result from two facts: 1. water is one of the smallest quantities (<2%) being balanced; 2. water requires more data (11) for balance calculations than any other.
4. As may be expected, weight balance and ash balance yield the most accurate and precise data.

### PROCEDURE

A Fischer assay is run in the usual manner (Method P-S-01) except that the evolved gas is trapped (see Figure V-A-1) and analyzed and the retorted shale retained for analysis (see Table V-A-1). Using acidified water in the gas collection bottle, about 1-2" of water vacuum is maintained throughout the assay. Twenty-nine analyses are needed to calculate nine balances: weight, ash, carbonate, kerogen, water, total C, total H, total N, and total S.

### DISCUSSION

The calculations used to determine the nine material balances are



A. FISCHER ASSAY MATERIAL BALANCES

CONCLUSIONS

1. Nine material balances were calculated on four Fischer assays. They included: weight, ash, carbonate, hydrogen, water, total carbon, total hydrogen, total nitrogen and total sulfur. All raw data and calculations are given.
2. Mean balances range from 97.1 to 106.9%; individual balances range from 90.0 to 119.5%. The need for multiple data points is obvious.
3. Only the water balance shows extreme deviations (106.9 ± 10.0%). The deviations result from two factors: 1. water is one of the smallest quantities (<5%) being balanced; 2. water requires more data (11) for balance calculations than any other.
4. As may be expected, weight balance and ash balance yield the most accurate and precise data.

PROCEDURE

A Fischer assay is run in the usual manner (Method P-2-01) except that the evolved gas is trapped (see Figure V-4-1) and analyzed and the reformed shale retained for analysis (see Table V-4-1). Using acidified water in the gas collection bottle, about 1-2" of water vacuum is maintained throughout the assay. Twenty-nine analyses are needed to calculate nine balances: weight, ash, carbonate, hydrogen, water, total C, total H, total N, and total S.

DISCUSSION

The calculations used to determine the nine material balances are

given in Tables V-A-2 and 3. Mean balances and their standard deviations are listed in Table V-A-4. The overall mean balance is 99.4%. Many of the "in" data are simply raw data on the raw shale charge. The Paraho standard raw shale was used for these studies; data used are the means reported in the STATISTICS section of the final report.

Weight Balance. This balance is simply the ratio of materials out (retorted shale, oil, water and gas) to materials in (raw shale). Although five raw data are needed, the values are large so that the weight balance is generally good.

Ash Balance. This balance is simply the ratio of the ash out to the ash in.

Carbonate Balance. For the Fischer assay, this balance is simply the ratio of the mineral  $\text{CO}_2$  out to the mineral  $\text{CO}_2$  in. Little or no carbonate decomposition occurs during Fisher assay retorting.

Kerogen Balance. This is one of the more complex balances. Kerogen in is calculated to be anything that is not inorganic (raw shale less mineral  $\text{CO}_2$ , ash, and water). Kerogen out is calculated to be all the organic products (coke, oil, and dry gas).

Water Balance. The water balance is one of the most complex balances. Water in is calculated to be the difference between anything that is not water in raw shale (raw shale less mineral  $\text{CO}_2$ , ash, coke, oil, and dry gas). Water out is the sum of normal Fischer assay water and moisture in the gas. Moisture in the oil is not considered in these balances. It is



given in Tables V-A-5 and 6. Mean balances and their standard deviations are listed in Table V-A-4. The overall mean balance is 99.4%. Many of the "in" data are simply raw data on the raw shale charge. The Petro standard raw shale was used for these studies; data used are the means reported in the STATISTICS section of the final report.

Weight Balance. This balance is simply the ratio of materials out (restored shale, oil, water and gas) to materials in (raw shale). Although live raw data are needed, the values are large so that the weight balance is generally good.

Ash Balance. This balance is simply the ratio of the ash out to the ash in.

Carbonate Balance. For the Fischer assay, this balance is simply the ratio of the mineral  $CO_2$  out to the mineral  $CO_2$  in. Little or no carbonate decomposition occurs during Fischer assay restoring.

Ketogen Balance. This is one of the more complex balances. Ketogen in is calculated to be anything that is not inorganic (raw shale less mineral  $CO_2$ , ash, and water). Ketogen out is calculated to be all the organic products (coke, oil, and dry gas).

Water Balance. The water balance is one of the most complex balances. Water in is calculated to be the difference between anything that is not water in raw shale (raw shale less mineral  $CO_2$ , ash, coke, oil, and dry gas). Water out is the sum of normal Fischer assay water and moisture in the gas. Moisture in the oil is not considered in these balances. It is

assumed that the water vapor in the gas originates from the retort and not the leveling fluid.

Carbon and Sulfur Balances. Both these balances are simple and straight forward. Material in is based on the direct analysis of the raw shale. Material out is based on the direct analyses of retorted shale, oil, and gas. It is assumed that little or no carbon or sulfur is in the Fischer assay water.

Hydrogen Balance. This balance is similar to the carbon and sulfur balances except that the theoretical hydrogen in the Fischer assay water is included in hydrogen out figure.

Nitrogen Balance. This balance is similar to the hydrogen balance except the ammonia nitrogen is measured in the Fischer assay water and the gas (including the acidified water used to maintain vacuum during the assay). It is assumed that all the nitrogen, liberated during the Fischer assay, exists as ammonia in the Fischer assay water and gas.

Gas. The gas collected during the Fischer assay is analyzed by gas chromatography for Fischer assay balance data. The gas compositions, quantity, and gross heating values are compared with USBM RI 4825 data in Table V-A-5. The mean data from this study show a mean gas yield of 560 SCF/T and a mean gross heating value (air-free basis) of 962 Btu/SCF.



# WESTON BOND

PERMANENT  
5% COTTON FIBER

TABLE V-A-1

FISCHER ASSAY BALANCE - ANALYTICAL DATA

Designation		(Analytical Data (in gm. expressed on basis of 100 gm raw shale))			
No.	Analysis	I	II	III	IV
1	<u>Raw Shale</u>	100.00			
2	Min CO <sub>2</sub>	17.40			
3	Ash	66.25			
4	Total C	17.49			
5	H	1.86			
6	N	0.53			
7	S	0.69			
8	<u>Retorted Shale</u>	85.26	85.13	85.00	85.56
9	Min CO <sub>2</sub>	17.80	16.83	16.75	18.05
10	Ash	65.75	65.32	65.50	66.57
11	Total C	6.88	6.92	6.96	6.90
12	H	0.196	0.187	0.187	0.188
13	N	0.298	0.294	0.306	0.282
14	S	ND	ND	ND	0.532
15	Coke	2.03	2.33	2.39	1.98
16	<u>Oil</u>	10.76	10.99	11.04	10.42
17	Total C	9.11	9.37	9.29	8.80
18	H	1.147	1.299	1.258	1.250
19	N	0.225	0.215	0.230	0.152
20	S	ND	ND	ND	0.080
21	<u>Gas</u>	1.834	2.040	2.115	2.033
22	Total C*	0.999	1.163	1.153	0.994
23	H*	0.177	0.248	0.212	0.228
24	(NH <sub>3</sub> ) N	ND	ND	ND	0.021
25	(H <sub>2</sub> S) S	ND	ND	ND	0.089
26	Water*	0.054	0.059	0.086	0.073
27	<u>Water</u>	1.35	1.36	1.62	1.50
28	Total H	0.150	0.151	0.180	0.167
29	(NH <sub>3</sub> ) N	0.006	0.005	0.007	0.008

ND = not determined

\*Based on theoretical concentrations from GC analysis.



TABLE V-A-1

VICTOR ARMY BALANCE - ANALYTICAL DATA

No.	Description	(Analytical Data) in % expressed on basis of 100 mg raw			
		I	II	III	IV
1	Raw Shale	100.00			
2	Raw CG	17.40			
3	Raw	66.12			
4	Total C	17.40			
5	H	1.66			
6	N	0.23			
7	S	0.69			
8	Reported Shale	82.26	82.12	82.00	82.24
9	Raw CG	17.80	16.43	16.78	16.06
10	Raw	68.72	65.32	62.20	66.27
11	Total C	6.88	6.92	6.96	6.96
12	H	0.188	0.187	0.187	0.188
13	N	0.298	0.294	0.298	0.292
14	S	NO	NO	NO	0.412
15	Calc	2.03	2.33	2.23	1.98
16	Oil	10.76	10.99	11.04	10.42
17	Total C	9.11	9.27	9.29	8.80
18	H	1.147	1.299	1.228	1.229
19	N	0.225	0.212	0.230	0.182
20	S	NO	NO	NO	0.080
21	Calc	1.828	2.040	2.162	2.093
22	Total C*	0.792	1.167	1.173	0.994
23	H*	0.177	0.248	0.212	0.228
24	(NH <sub>4</sub> ) <sub>2</sub> S	NO	NO	NO	0.031
25	(NH <sub>4</sub> ) <sub>2</sub> S	NO	NO	NO	0.089
26	Water*	0.021	0.022	0.026	0.023
27	Water	1.22	1.36	1.42	1.20
28	Total H	0.120	0.121	0.180	0.167
29	(NH <sub>4</sub> ) <sub>2</sub> S	0.008	0.002	0.007	0.006

NO = not determined

\*Based on theoretical concentrations from C analysis

TABLE V-A-2

FISCHER ASSAY BALANCE - CALCULATED DATA

Designation			I	II	III	IV
<u>Letter</u>	<u>Value</u>	<u>Calculations</u> <sup>(1)</sup>				
A.	Weight Out	8+16+21+27	99.20	99.52	99.78	99.51
B.	Kerogen In	1-2-3-27	15.00	14.99	14.73	14.85
C.	Kerogen Out	15+16+21-26	14.57	15.30	15.46	14.36
D.	Water In <sup>(2)</sup>	1-2-3-15-16-21+26	1.428	1.428	1.428	1.428
E.	Water Out	26+27	1.404	1.419	1.706	1.573
F.	Carbon Out	11+17+22	16.99	17.45	17.40	16.69
G.	Hydrogen Out	12+18+23+28	1.670	1.885	1.837	1.833
H.	Nitrogen Out	13+19+24+29	0.550	0.535	0.564	0.463
J.	Sulfur Out	14+20+25	---	---	---	0.701

(1) Numbers refer to Table V-A-1

(2) Average of all four runs.



Part 1

TABLE V-A-2  
FISCHER ASSAY BALANCE - CALCULATED DATA

Factor	Designation		Calculations (1)	I	II	III	IV
	Value	Value					
A.	Weight Out	6+16+21+27		39.36	39.32	39.78	39.21
B.	Ketogen In	1-2-3-27		12.00	14.99	14.73	14.82
C.	Ketogen Out	12+16+21-28		14.27	12.30	12.46	14.36
D.	Water In (2)	1-2-3-15-16-21+26		1.428	1.428	1.428	1.428
E.	Water Out	26+27		1.404	1.419	1.706	1.273
F.	Carbon Out	11+17+22		16.92	17.42	17.40	16.88
G.	Hydrogen Out	12+16+23+28		1.670	1.892	1.817	1.893
H.	Nitrogen Out	13+19+24+29		0.520	0.522	0.564	0.462
J.	Sulfur Out	14+20+25		---	---	---	0.701

(1) Numbers refer to Table V-A-1

(2) Average of all four runs.

TABLE V-A-3

FISCHER ASSAY BALANCES

Balance	Calculation <sup>(1)</sup>	I	II	III	IV
Weight	A/1	99.2	99.5	99.8	99.5
Ash	10/3	99.2	98.6	98.9	100.5
Carbonate	9/2	102.3	96.7	96.3	103.7
Kerogen	C/B	97.1	102.1	105.0	96.7
Water	E/D	98.4	99.4	119.5	110.2
Carbon	F/4	97.1	99.8	99.5	95.4
Hydrogen	G/5	90.0	101.3	98.8	98.5
Nitrogen	H/6	103.8	100.9	106.4	87.4
Sulfur	J/7	---	---	---	101.6

(1) Numbers refer to Table V-A-1 and letters to Table V-A-2.

(2) Means plus or minus one standard deviation.



TABLE V-A-3

STINGER ARMY BALANCES

Balance	Calculation (1)	I	II	III	IV
Weight	AW	99.2	99.2	99.8	99.2
Asb	10/3	99.2	98.2	98.2	100.2
Carbonate	9/2	102.2	96.7	96.1	102.7
Hydrogen	Q/R	97.1	102.1	102.0	96.7
Water	R/D	98.4	92.4	112.2	110.2
Carbon	7/4	97.1	92.8	92.2	92.4
Hydrogen	Q/2	90.0	101.7	92.8	98.2
Water	R/2	102.8	100.9	102.2	97.4
Sulfur	2/3	---	---	---	101.2

(1) Numbers refer to Table V-A-1 and letters to Table V-A-2.





TABLE V-A-4

COMPOSITE FISCHER ASSAY BALANCES

WEIGHT	$99.2 \pm 0.24$
ASH	$99.3 \pm 0.36$
CARBONATE	$99.7 \pm 3.88$
NITROGEN	$100.2 \pm 4.06$
WATER	$106.3 \pm 10.06$
CARBON	$98.0 \pm 2.12$
HYDROGEN	$97.2 \pm 4.92$
NITROGEN	$99.6 \pm 8.22$
SULFUR	101.6

(1) Means plus or minus one standard deviation.

TABLE V-A-5  
GAS COMPARISON DATA

Gas, dry, air-free, 60°F, 30"Hg CF/T	<u>PARAHO</u>				Ave.	<u>USBM<sup>(1)</sup></u>		Ave.
	Run 1	Run 2	Run 3	Run 4		Min.	Max.	
Btu/CF					556			516
Vol%					962			832
H <sub>2</sub>	24.8	19.6	23.0	29.6	24.3	13.7	25.7	22.3
CO	5.2	4.7	4.6	4.9	4.8	0.0	6.8	3.1
CH <sub>4</sub>	20.7	18.7	18.7	18.7	19.2	15.2	21.6	17.9
CO <sub>2</sub>	24.9	24.4	24.9	23.2	24.3	21.8	45.8	29.7
C <sub>2</sub> H <sub>4</sub>	3.8	3.1	2.8	2.4	3.0	1.6	3.3	2.2
C <sub>2</sub> H <sub>6</sub>	6.5	6.8	6.3	6.5	6.5	5.3	9.3	7.1
C-3's	5.0	8.7	8.3	6.2	7.0	3.5	8.7	5.7
C-4's	6.6	7.4	6.8	3.6	6.1	3.8	5.5	3.8
C-5's	1.8	3.5	2.5	1.4	2.3	1.3	2.9	1.9
C-6's	0.4	1.0	0.8	0.6	0.7	0.7	2.0	1.3
H <sub>2</sub> S	0.4	2.0	1.3	1.9	1.4	0.0	7.7	3.2

(1) Reprinted from Bureau of Mines Report of Investigations 4825.



TABLE V-2-2

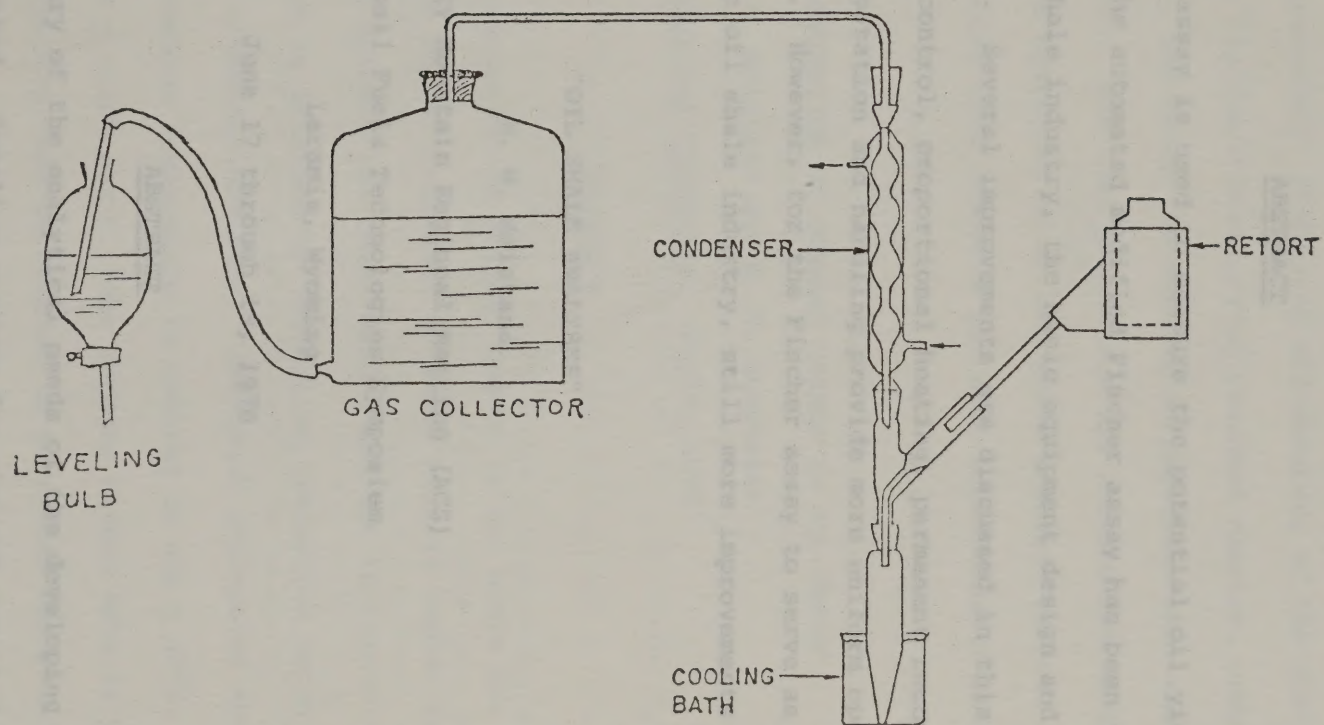
GAS COMPOSITION DATA

Gas, dry, air-free, CO <sub>2</sub> , 30 in Hg	Run 1	Run 2	Run 3	Run 4	Avg.	Range	
						Min.	Max.
H <sub>2</sub>	15.8	15.8	15.0	20.5	16.3	13.7	22.7
CO	2.5	4.7	4.8	4.8	4.8	0.0	11.1
CH <sub>4</sub>	20.7	18.7	18.7	18.7	19.2	12.2	27.9
CO <sub>2</sub>	24.8	24.4	24.8	24.2	24.3	21.8	29.7
C <sub>2</sub> H <sub>6</sub>	3.8	3.1	3.8	3.4	3.0	1.8	7.3
C <sub>2</sub> H <sub>4</sub>	6.2	6.8	6.3	6.3	6.2	2.1	11.1
C-1's	2.0	0.7	0.3	0.2	0.0	0.2	2.7
C-2's	0.6	0.4	0.8	0.6	0.1	0.0	2.8
C-2's	1.8	1.2	1.8	1.4	1.3	1.3	1.9
C-3's	0.4	1.0	0.8	0.6	0.7	0.7	1.3
H <sub>2</sub> S	0.4	2.0	1.3	1.9	1.4	0.0	3.3

(1) Regulated from Bureau of Mines report of investigation 4852.

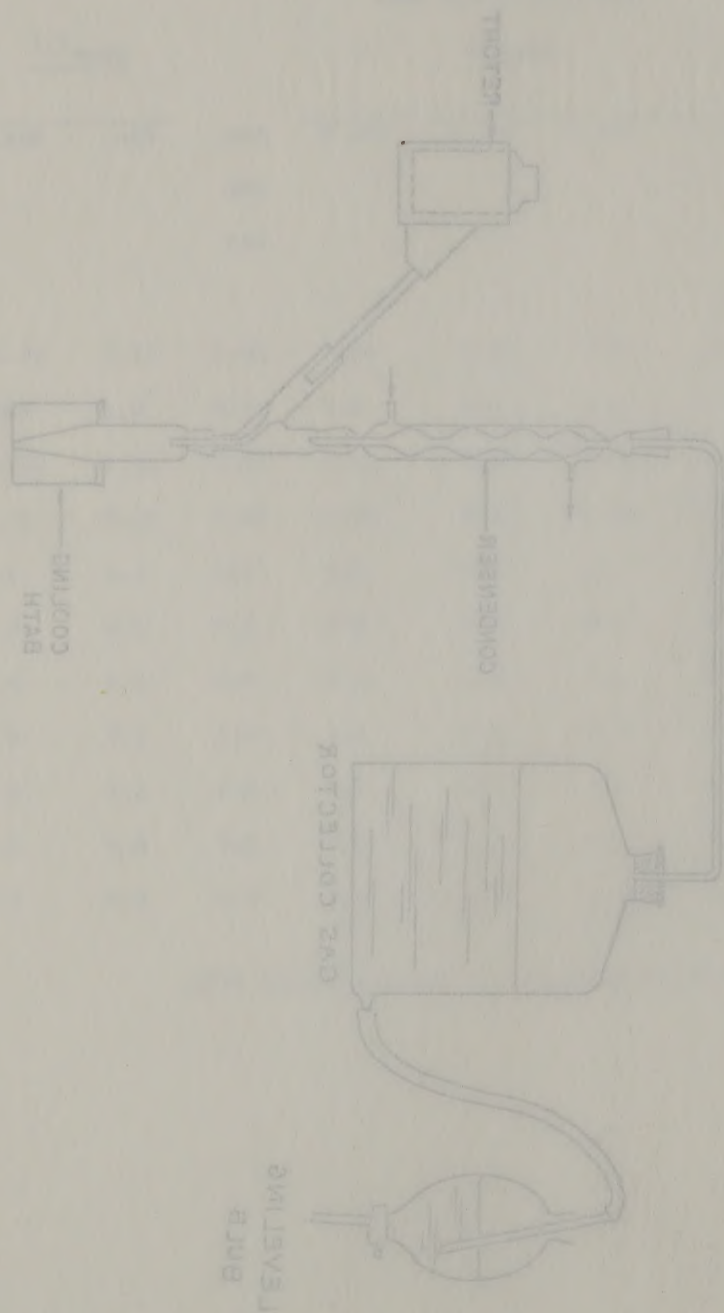
FIGURE- 5-1

MODIFIED FISCHER ASSAY APPARATUS



USBM RI 6676 (1965)





10-10

10-10

## "THE FISCHER ASSAY - STANDARD FOR THE OIL SHALE INDUSTRY"

R. N. Heistand

Energy Sources, 2 (4), 397, (1976)

### ABSTRACT

The Fischer assay is used to measure the potential oil yield from oil shale. Although the automated modified Fischer assay has been the standard for the oil shale industry, the basic equipment design and procedure need improvements. Several improvements are discussed in this paper. The use of continuous control, proportional heating, permanent recording and careful sample preparation and handling provide more uniform operation and more reliable data. However, for the Fischer assay to serve as the standard for the future oil shale industry, still more improvements will be needed.

## "OIL SHALE ANALYSES"

R. N. Heistand

Rocky Mountain Regional Meeting (ACS)

Fossil Fuels Technologies Symposium

Laramie, Wyoming

June 17 through 19, 1976

### ABSTRACT

A brief summary of the analytical needs of the developing oil shale industry is presented. Sampling systems for raw and retorted oil shale, recycle gas, and crude shale oil are illustrated. Details of the



# "THE FISCHER ASSAY - STANDARD FOR THE OIL SHALE INDUSTRY"

A. M. Weinstand

Energy Sources, 3 (4), 197 (1976)

## ABSTRACT

The Fischer assay is used to measure the potential oil yield from oil shale. Although the automated modified Fischer assay has been the standard for the oil shale industry, the basic equipment design and procedures need improvements. Several improvements are discussed in this paper. The use of continuous control, proportional heating, permanent recording and careful sample preparation and handling provide more uniform operation and more reliable data. However, for the Fischer assay to serve as the standard for the future oil shale industry, still more improvements will be needed.

## "OIL SHALE ANALYSIS"

A. M. Weinstand

Rocky Mountain Regional Meeting (ACSI)

Fossil Fuels Technology Symposium

Laramie, Wyoming

June 17 through 19, 1976

## ABSTRACT

A brief summary of the analytical needs of the developing oil shale industry is presented. Sampling systems for raw and retorted oil shale, retorted gas, and crude shale oil are illustrated. Details of the

routine tests are discussed along with the useful applications of these analytical data. "Typical data" obtained from these tests are given. Various environmental tests applied to stack emissions and ground, surface, and product water are presented. Precision and accuracy of the routine tests were evaluated by replicate analyses of standard samples, comparisons with other laboratories, and using the obvious correlations that exist among oil shale test data. The test procedures and information discussed in this paper represent the operation of an oil shale research project. The tests will certainly become more numerous and more sophisticated as the oil shale industry matures.

# "DIRECT DETERMINATION OF ORGANIC CARBON IN OIL SHALE"

R. N. Heistand and H. B. Humphries

Analytical Chemistry, (8),1192,1976

## ABSTRACT

A direct determination of organic carbon in oil shale has been developed to replace the normal procedure in which organic carbon is calculated as the difference between the total carbon and the inorganic carbon. The direct determination is obtained by controlled combustion using the Perkin-Elmer Model 240 Elemental Analyzer. Inorganic carbonates are not pyrolyzed when the combustion temperature is lowered to  $450 \pm 10^{\circ}\text{C}$ . Precision of the method is  $\pm 0.10\%$  org C. The organic carbon data is useful in raw shale characterization, can be related to potential oil yield, and serves as a measure of energy potential, or coke, remaining on the retorted shale.



routine tests are discussed along with the useful applications of these analytical data. "Typical data" obtained from these tests are given. Various environmental tests applied to stack emissions and ground, surface, and product water are presented. Precision and accuracy of the routine tests were evaluated by replicate analyses of standard samples, comparisons with other laboratories, and using the obvious correlations that exist among oil shale test data. The test procedures and information discussed in this paper represent the operation of an oil shale research project. The tests will certainly become more numerous and more sophisticated as the oil shale industry matures.

"DIRECT DETERMINATION OF ORGANIC CARBON IN OIL SHALE"

R. N. Halstead and H. E. Humphries  
*Analytical Chemistry*, (8), 1192, 1976

ABSTRACT

A direct determination of organic carbon in oil shale has been developed to replace the normal procedure in which organic carbon is calculated as the difference between the total carbon and the inorganic carbon. The direct determination is obtained by controlled combustion using the Perkin-Elmer Model 140 Elemental Analyzer. Inorganic carbonates are not pyrolyzed when the combustion temperature is lowered to  $450 \pm 10^\circ\text{C}$ . Precision of the method is  $\pm 0.10\%$  org C. The organic carbon data is useful in raw shale characterization, can be related to potential oil yield, and serves as a measure of energy potential, or coke, remaining on the retorted shale.

"THE FISCHER ASSAY, A STANDARD METHOD?"

R. N. Heistand

Symposium on Coal, Oil Shale, and Tar Sands

Division of Fuel Chemistry

National ACS Meeting, San Francisco, CA

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ABSTRACT

The Fischer assay is a performance test rather than a quantitative analytical procedure. As such, the data obtained from a Fischer assay are quite dependent upon the test procedure. The standard USBM Fischer assay, as described in Report of Investigation 6676, has been modified by most laboratories performing this test. These modifications, variations of procedures permitted in the USBM method, and some of the procedures suggested in the USBM method do indeed cause errors and wide variations in the Fischer assay data. Suggestions for correcting some of these inconsistencies and improving the Fischer assay are offered in these areas: sampling, mesh size, retort design, temperature of retort, condenser and receiver. Since most of the alternatives proposed to replace the Fischer assay have serious shortcomings, a standard Fischer assay test procedure is needed for the oil shale industry.





## VI. RECOMMENDATIONS AND CONCLUSIONS

Based on experience in the Paraho Laboratory, there are three recommendations to provide more data, more reliably, with more efficient use of personnel, time and funds. These recommendations are:

1. employ continuous monitors whenever possible;
2. automate analyses and data acquisition whenever possible;
3. broaden the laboratory function in two directions --

retort operations and data handling. This will help insure that more meaningful samples are obtained, that the laboratory tests answer the question in mind, and that data handling distinguish between real differences and noise.

The laboratory, like the other aspects of the Paraho project, was faced with three problems. The first -- operating constantly on a "learning growth curve" -- meant that routine sampling and testing procedures were improved as knowledge was gained. The second problem -- operating in a restricted time frame with restricted capital funds -- is simply aspects of the Paraho project that permitted attainment of program funding. This prevented the purchase of expensive or long-delivery equipment needed to improve and expedite the laboratory work. The third -- adapting existing facilities and equipment -- is a result, primarily of the former problem. This last problem caused more maintenance resulting in less efficiency than had been expected for routine laboratory operations.

Comments concerning the individual samples and test follow ...



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Comments concerning the individual samples and test follow ...

Raw Shale. The raw shale sampling system worked well throughout the project. Valid, representative samples were obtained in quantity and mesh size easily handled by the laboratory. The determination of total sulfur should be added to the routine tests. Sampling could be reduced to once-a-day, but, because of poor precision, the Fischer assay should be done in duplicate. A better procedure for the sampling and determination of moisture on the raw shale feed would be welcomed. A rapid alternative for the Fischer assay oil yield (gal/ton) and water yield (gal/ton) would provide better control of retorting operations.

Retorted Shale. For the most part, comments made for raw shale concerning the sampling system and routine tests also apply for retorted shale. Experience has shown that both shale sampling systems work better when the feeders and crushers operate continuously. Less blockages occur during continuous operations than when the gross sample is stored during the entire sampling period. For retorted shales, continuous operation also minimized the oxidation loss of organic carbon by eliminating the storage of the gross sample of hot retorted shale for the entire sampling period.

The Fischer assay of retorted shale does not have the quantitative nature of the raw shale data. That is, the Fischer assay of retorted shale is a screening test to assure complete oil removal in retort operations. Thus, duplicate tests are not needed for retorted shale.

Oil. The oil sampling system, using agitation and bottom-to-top recirculation, provided representative samples of wet product oil when water content was less than 10 wt%. For samples having more water, a separation step is needed. Because of difficulties in sampling and handling and because precise water contents are needed, a continuous



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 handling and because precise water contents are needed, a continuous

in-line monitor for water in oil is suggested.

Water is the only oil test that affects yield and balance data. Since water is also the only test that varies widely, the other tests could be run on composite samples from larger storage tanks. Additional tests that should be run routinely on this composite sample include total sulfur, pour point (A.S.T.M. D-97) and atmospheric distillation (A.S.T.M. D-86).

Recycle Gas. Sampling recycle gas for the routine laboratory tests (Gas chromatography and condensate) has been the least satisfactory of all routine samples. Flooded or plugged sample lines and questionable results were too common. Based on the reliable performance of the on-stream gas chromatograph, a more sophisticated model, with backflush capabilities to determine the C<sub>5</sub>+ naphthas, is needed.

Continuous on-stream monitors for water, hydrogen sulfide, and ammonia should be used to provide a sufficient quantity of valid data for these important parameters.

Characterization of the oil mist particle size and determination of the mist loading, is a time-consuming test. In order to improve the data by approaching isokinetic sampling more closely, additional sampling points should be located away from areas of turbulent flow. Measurement of the gas velocity in the cross-sectional area at the sampling point should be done before mist characterizations and measurements are done.



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Measurement of the gas velocity in the cross-sectional area at the

sampling point should be done before mist characterizations and measurements

are done.

Water. Process water, obtained either with the product oil or as a condensate from recycle gas, should be sampled and analyzed for ammonia, carbonate (bi-carbonate) and organic carbon. Because these samples were not obtained on a routine basis, no valid recommendations concerning sample procedures, frequency, or analyses can be made at this time. The results of these samples should provide additional data for the water, kerogen, organic carbon, and organic nitrogen balances.

Environmental. In-stack continuous monitors should be installed in the thermal oxidizer, or any stack where effluents of combustion of shale oil or gas are emitted, to measure common pollutants. These include sulfur dioxide, oxides of nitrogen, carbon monoxide, hydrocarbons and particulates.

Monitoring ground and surface water to assess effects of gross salinity, hydrocarbon contamination, and possible toxic materials should be continued. The frequency and scope of the monitoring program used during the Paraho project appear to be acceptable.

A meteorological station should be maintained. Information on temperature, barometric pressure, relative humidity, rainfall, evaporation, wind direction and wind speed should be obtained.

Data Acquisition. With the increased data obtained from numerous continuous on-stream monitors, automated data acquisition, storage and handling is needed. Automation in this area would permit more thorough monitoring of the retort temperature and pressure.



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